Synthetic and Physical Organic Studies on Metal Complexes of Cyclopropenylidenes(Dissertation_全文)

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PREFACE

The studies presented in this thesis have been carried out under the direction of Professor Zen-ichi Yoshida at the Department of Synthetic Chemistry of Kyoto University during 1976 - 1980.

The author wishes to express his grateful gratitude to Professor Zen-ichi Yoshida. His continuous encouragement and kind guidance are deeply appreciated. The author is also sincerely grateful to Professor Hisanobu Ogoshi, Professor Shigeo Yoneda and Assistant Professor Yoshinao Tamaru for their helpful discussions and comments. The author is further greatly indebted to Assistant Professor Hisatoshi Konishi for his introduction and contribution to this studies. Furthermore, the author's thanks are due to Dr. Sadao Miki, Dr. Hiroshi Sugimoto and Dr. Tokuzo Kawase for their valuable advices and discussions. The author also wishes to express his sincere thanks to Professor James A. Ibers for his active collaborations on X-ray crystallographic studies. The author is also greatly indubted to Dr. Teizo Kitagawa for the measurements of resonance Raman and far-infrared spectra. Sincere thanks are extended to Professor Masaru Hojo for his helpful suggestions on the correction of English expression in this thesis. Valuable suggestions, kindness and goodwills of the author's colleagues are greatfully acknowledged.

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Yasuhiro Kamitori

June 1981.

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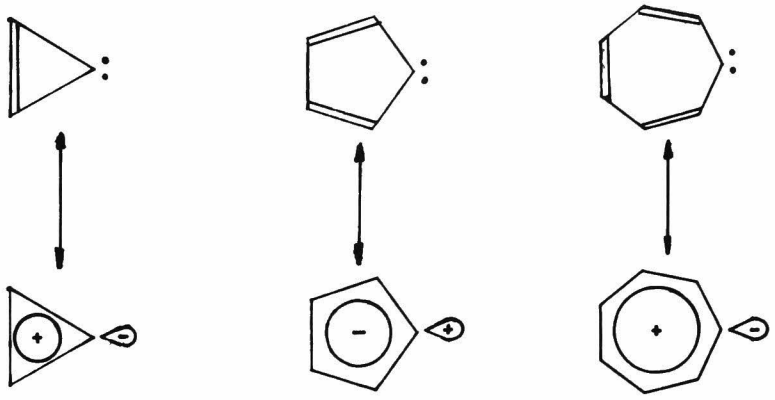
INTRODUCTION

Highly strained molecules have attracted interests of chemists from theoretical as well as synthetic aspects and a number of papers have been published to reveal their interesting behaviors. During the last three decades the chemistry of cyclopropenium ions as one of the most important members in this class has been developed extentively, providing valuable informations about concepts of chemical bonding, aromaticity, hybridization, strain energy and so on.

Since the first cyclopropenium cation,[1] was successfully prepared by Breslow, a number of related derivatives have been synthesized. A current of these investigations has opened several new fields of chemistry, in which cyclopropenes, cyclopropenones, a new cross-conjugated π-electron system represented by calicene and its analogues together with their synthetic applications are involved.

In addition recent rapid developements in both synthetic techniques and spectroscopic instrumentations have prompted the chemists to synthesize very active and unstable species whose novelties have been predicted by several quantum chemists. Cyclopropenylidene 1 is one of such species.

Conjugated cyclic carbenes can be classified into two groups,[2] i.e., 4nπ carbenes represented by cyclopentadienylidene 2[3] and (4n+2)π carbenes such as cyclopropenylidene 1 and cycloheptatrienylidene 3.[4] (4n+2)π Carbenes are characterized by their relative large S_0-T_1 gap while 4nπ carbenes are estimated to have triplet ground state.[5] As the simplest (4n+2)π carbene, cyclopropenylidene possesses

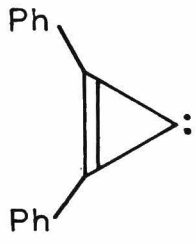


1 2 3

very strained bent bonds in its framework and is believed to have one of the largest S_0-T_1 gap[5] due to 2π aromaticity of the C-3 ring.

In spite of the well predicted properties from MO calculations,[5 - 10] real structure of cyclopropenylidene still remains unknown. In addition, generation and reactions of cyclopropenylidene have been reported only with its bisphenyl derivative 4 by Jones and his co-workers[11-15] and no definite evidence is available for the generation of unsubstituted cyclopropenylidene. Because of its instability, it is difficult to characterize such a species even by spectroscopic methods.

On the other hand, a variety of cyclopropenium cations which are stabilized by peripheral electron donating substituents such as amino groups have been synthesized. On the basis of these investigations, Yoshida and Konishi have succeeded in preparing carbenoid species (5, 6)[16,17] of bisaminocyclopropenylidene. The nature of carbenoid 5 as well as bisaminocyclopropenylidene 7 itself seems to be an



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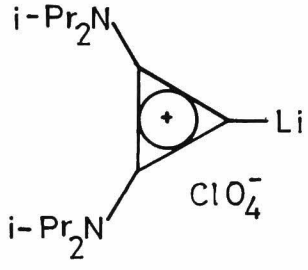

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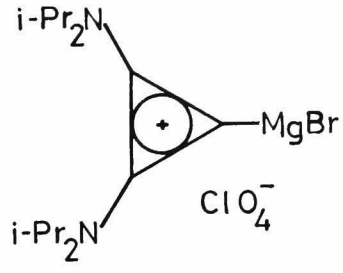

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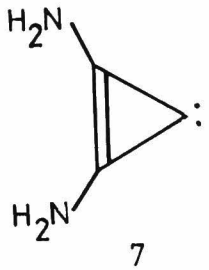
interesting research subject in the chemistry of cyclopropenylidene.

In Chapter 1 are described properties of bisaminocyclopropenylidenes predicted from extended Hückel and MINDO/3 MO calculations, together with reactions and ^{7}Li-NMR spectrum of carbenoid 5. As is seen from 1, bisaminocyclopropenylidene is thought to be very nucleophilic and have characters close to carbanions. Such a strong nucleophilicity is actually observed in the reactions of bisaminocyclopropenylidene lithium 5, and its ^{7}Li-NMR spectrum also suggests corresponding ionic character of C - Li bond of 5. Thus carbenoid 5 should be near in its character to bisaminocyclopropenylidene itself. Nucleophilic reactions of 5 are usefully applicable to preparations of a wide variety of new organic and organometallic three-memberd ring compounds.

Carbenoid 5 is considerably stabilized by the peripheral amino substituents but not so stable as to be isolated. Taking account of many successful isolations of carbenes as transition metal complexes[18] such as 8, cyclopropenylidene transition metal complexes 9 are thought to have sufficient stability for studying their structures.



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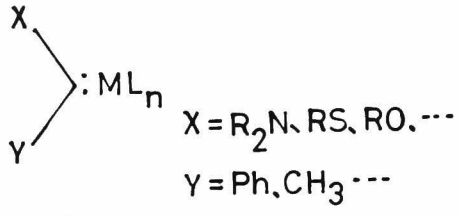

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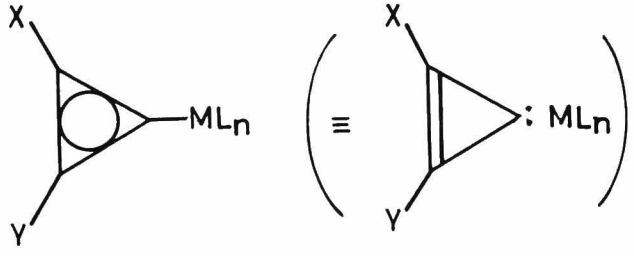

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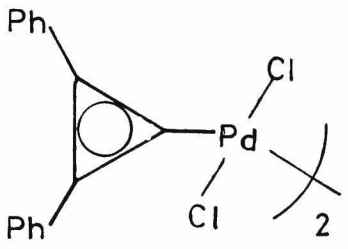
The research on cyclopropenylidene transition metal complexes must provide us valuable **information** for the nature and structure of cyclopropenylidene itself. In addition, properties of cyclopropenylidene moiety as a highly strained organic ligand seems very interesting from the standpoint of organometallic chemistry.

The first example of such a type of complex was reported by Öfele[19,20] about palladium^{II} and chromium^{0} complexes 10, 11. However subsequent structural study[21] for these compounds is of no sufficient accuracy to clarify the nature of these cyclopropenylidene complexes. In the present investigation, a variety of transition metal complexes of cyclopropenylidenes were synthesized and their characteristics were studied systematically.



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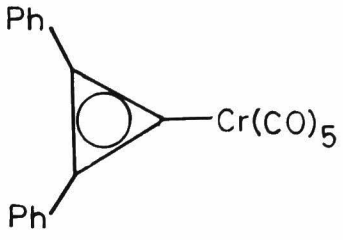

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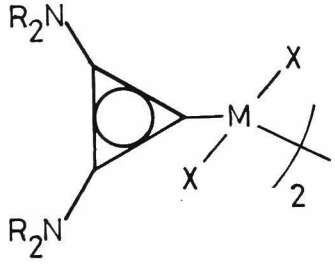
In Chapter 2 are described syntheses and properties of square planar type transition metal(Pd, Pt, Rh) complexes(12, 13, 14) of diverse bisaminocyclopropenylidenes. These very stable complexes were prepared by either oxidative addition of bisamino-halocyclopropenium halide to zerovalent metals or direct metal exchange reaction of bisaminocyclopropenylidene lithium 5 with several other transition metal complexes.



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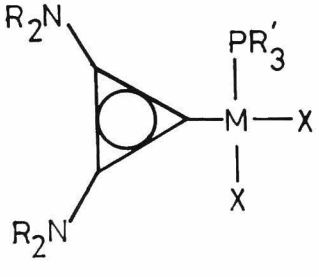

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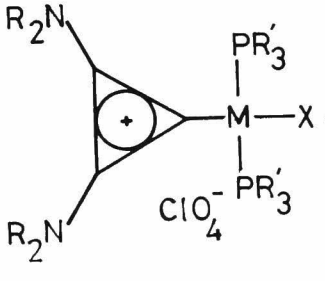

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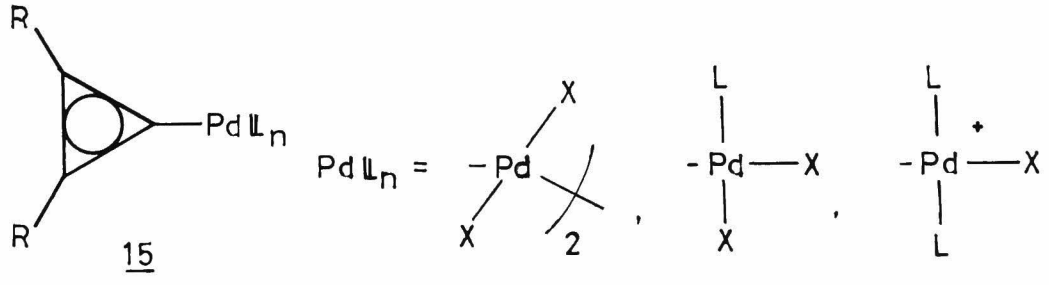
In Chapter 3 is described X-ray crystallographic study of bisaminocyclopropenylidene palladium. Equivalence of bond distances within the C-3 ring and relatively short C_{ring}-N and C_{ring}-Pd bonds

were observed, which suggest considerable π-back donation from metals to C-3 ring, comparable in its effect to the conjugative interaction between amino groupes and the cyclopropenylidene core. This strong π-back bonding and consequent slight loosening of each C_{ring}-C_{ring} bond are thus interpreted as the result of interactions between metal 4d-5p orbitals and cyclopropenylidene molecular orbitals, energy levels of which are near to nonbonding level.

In Chapter 4 are **presented** synthesis and properties of bisalkylcyclopropenylidene palladium complexes 15, the first example of stable transition metal complexes containing bisalkylcyclopropenylidene moiety. In such cyclopropenylidene complexes which have no strong electron donating substituents such as amino groups, more significant contribution of metal π-back bonding and 2π aromaticity of the C-3 ring are expected.



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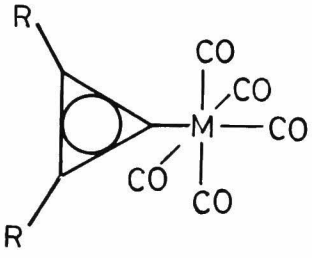
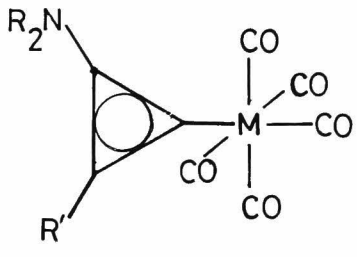
Although syntheses and chemical properties of cyclopropenethiones[22] and cyclopropeneselones[23] have been reported, reactions of these species with transition metal complexes are still unknown.

In Chapter 5 are recorded syntheses and properties of pentacarbonyl (Cr, Mo, W)complexes of diverse cyclopropenylidene 16 - 21. Pentacarbonyl complexes of bisamino-, amino(thio)-, amino(phenyl)cyclopropen-

ylidenes(18, 20, 21) were synthesized in high yields through novel desulfurization reactions of cyclopropenethiones. Similarly the first complexes which contain bisthiocyclopropenylidene moieties 19, were prepared by deselenization reaction of bisthiocyclopropeneselone.

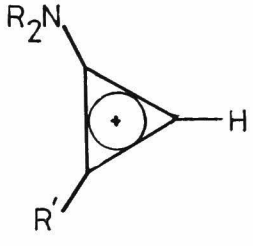


R	
i-Pr	16
Ph	17
R_2N	18
t-BuS	19



R′	
t-BuS	20
Ph	21

The complexes 20 and 21, on treatment with acid, afforded cyclopropenium cation 22 and 23, respectively.



R′	
t-BuS	22
Ph	23

In Chapter 6 are described spectroscopic studies of complexes 16 - 21 with the use of infrared, ^{13}C-NMR, and ^{17}O-NMR spectra. Electron densities on the C-3 ring were found in the order, 18 ≫ 19

> 17 > 16. Charge donating power and back charge acceptability of cyclopropenylidene ligands are also discussed.

In Chapter 7 are described the first measurements of ^{195}Pt- and ^{95}Mo-NMR spectra of cyclopropenylidene complexes, and chemical shifts and coupling constants in these complexes are discussed. These spectra were found to be very useful for structural elucidation of these transition metal complexes.

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CHAPTER 1

BISAMINOCYCLOPROPENYLIDENE-LITHIUM REACTIONS AND ^{7}Li-NMR SPECTRA

SUMMARY

Bisaminocyclopropenylidene is expected to be highly nucleophilic and have a character close to that of carbanions. Bis(di-i-propylamino)cyclopropenylidene lithium 1 was found to behave as a nucleophile toward various substrates. ^{7}Li-Chemical shift and approximated free energy of activation for Li - Li exchange of 1 suggest considerable ionicity of the $C_{carbene}$ - Li bond. These phenomena provide good evidences for 1 possessing a character considerably close to that of bisaminocyclopropenylidene itself.

INTRODUCTION

So far characteristic properties of cyclopropenylidene in ground as well as in excited states have been well predicted on the basis of MO calculations.[1-6] However there have been no reports dealing with substituted cyclopropenylidenes in which two peripheral substituents would perturb significantly the molecular orbitals of the ring in both ground and excited states.

In contrast, as for generation of cyclopropenylidenes, only few works are now available. Jones and his co-workers reported the chemistry of bisphenylcyclopropenylidene[7-11] but there seems to be no papers reporting definite evidence for the generation of free cyclopropenylidene. Because of its instability and high reactivity, it is difficult to characterize such a species even spectroscopically.

In this chapter is described my study on bis(di-i-propylamino)-cyclopropenylidene lithium 1 as a good substitute for cyclopropenylidenes. In particular, i) substituent effect for cyclopropenylidene systems predicted from extended Hückel and MINDO/3 MO calculations, ii) reactions of 1 with diverse organic and inorganic compounds, and iii) ^{7}Li-NMR spectra of 1 and some representative organic and inorganic lithium compounds, were studied.

RESULTS AND DISCUSSION

MO Calculations for Cyclopropenylidenes. Hoffmann discussed about Homo-Lumo splitting of conjugated cyclic carbenes and such a splitting were correlated with energy gap between conjugated p_z orbital

and isolated orbital perpendicular to p_z orbital of the carbene carbon.[1] Considerably large energy gap estimated for cyclopropenylidene means its existance as a singlet in the ground state, and higher electron density at the carbene carbon implies nucleophilic character of this species. As concluded by Hoffmann, several MO calculations suggest the most contributing canonical form in the ground state to be B.[2,3,6] When substituents X are electron donating groups, more stabilization can be expected for the canonical form B. In Table 1 are listed Homo-Lumo gaps estimated from extended Hückel MO calculation. The greatest energy gap for bisaminocyclopropenylidene also suggests dominant contribution of canonical form B.

As shown in Table 2, remarkably much **amount** of negative charge is at carbene carbon of bisaminocyclopropenylidene, either from extended Hückel or MINDO/3 MO calculations. This result coupled with the fact that introduction of two amino groups greatly stabilize cyclopropenium

Table 1 HOMO-LUMO gap, ΔE(eV) on several cyclopropenylidenes, X_2C_3: by extended Hückel MO calculations.

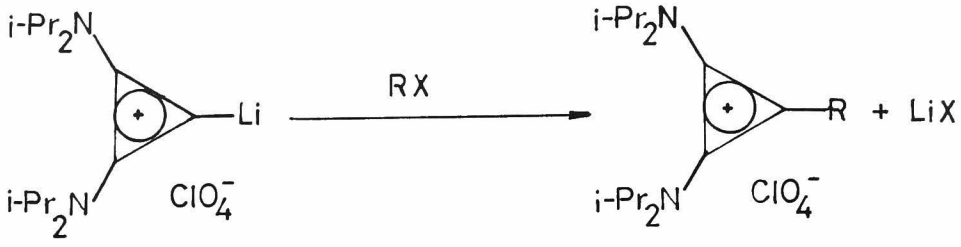
X	H	Me	Ph	HS	H_2N
ΔE	3.034	3.021	2.199	3.137	3.334

Table 2 Total charge density at carbene carbon on X_2C_3: estimated by extended Hückel and MINDO/3 MO calculations.

X	H	Me	Ph	HS	H_2N
Extended Hückel	-0.703	-0.865	-0.815	-0.990	-1.000
MINDO/3	-0.162	-0.159	-0.208	-0.211	-0.276

system means bisaminocyclopropenylidene should have a character close to that of carbanions.

Reactions of 1 As expected from the above calculation, 1 is actually very nucleophilic and reacts with a variety of electrophiles to afford corresponding products. These are summarized in Table 3 together with respective yields. These reactions can be utilized for preparations of many kinds of cyclopropenium cations. Among them, reaction of 1 with anhydrides and chlorides of carboxylic acids can give cyclopropenium cations in which electron withdrawing groups are directly linked to the cyclopropenium rings. In these cations, 2f-i are the first examples of stable cyclopropenium cations bearing electron withdrawing groups. Decarboxylations of 2g and i proceed quite easily in both acidic and basic conditions. Hydrolysis of 2g was examined in both 0.4 % K_2CO_3 aq. and 70 % $HClO_4$ aq. solutions. However, resulting product was not carboxylic acid 2l but decarboxylated product 2a. Similarly 2i treated with water and 70 % $HClO_4$ aq. solution gave only 2a. On the other hand thiolate 2j, a dipolar compound accessible by reaction of 1 and CS_2, is very stable even in the presence of moisture. Michael type reaction occurred when 1 was treated with an equimolar



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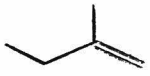
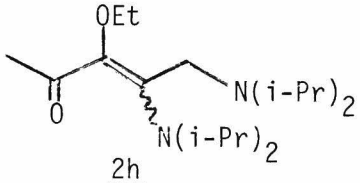
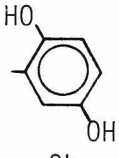
-R =	-H	-D	$-CH_3$		
	2a	2b	2c	2d	2e

-R =	$-COCH_3$	$-CO_2Et$		$-CO_2Li \cdot 2H_2O$
	2f	2g	2h	2i

-R =			$-CO_2H$	$-BF_3^-$
	2j	2k	2l	3

-R =	$-Pd(n\text{-}Bu)_3Cl$ $P(n\text{-}Bu)_3$	$-Pt(n\text{-}Bu)_3Cl$ $P(n\text{-}Bu)_3$	$-Rh(n\text{-}Bu)_3CO$ $P(n\text{-}Bu)_3$	$-Ti(\pi\text{-}C_5H_5)_2Cl$
	5a	5b	5c	6

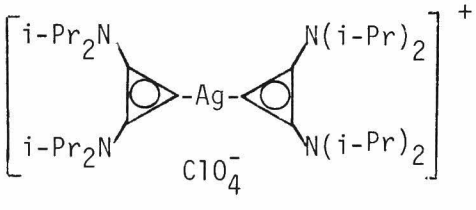


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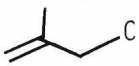
Table 3 Products and yields on the reactions of 1 with several reactants.

Entry	Reactants	Yields(%)	Products	
1	AcOD	98	2b	this work
2	CH_3I	72	2c	ref 12
3		56	2d	this work
4	PhCHO	59	2e	ref 12
5	Ac_2O	65	2f	this work
6	ClC_2Et	68	2g	this work
7	1/2 $ClCO_2Et$	31	2h	this work
8	CO_2	85	2i	this work
9	CS_2	27	2j	this work
10	OC_6H_4O	47	2k	this work
11	BF_3/ether	78	3	chapter 2
12	trans-$(n\text{-}Bu_3P)_2PdCl_2$	67	5a	chapter 2
13	trans-$(n\text{-}Bu_3P)_2PtCl_2$	58	5b	chapter 2
14	trans-$(n\text{-}Bu_3P)_2Rh(CO)Cl$	43	5c	this work
15	$(\pi\text{-}C_5H_5)_2TiCl_2$	34	6	this work
16	$AgSO_3CF_3$	67	7	this work

amount of benzoquinone, affording hydroquinone 2k. Reactions of 1 with Lewis acids and several organometallic compounds were also successfully performed. These reactions can be utilized for preparations of several cyclopropenylidene transition metal complexes, which will be definitly described in next chapter. Palladium, platinum, rhodium, titanium, and silver complexes of bisaminocyclopropenylidene, 5a-7, are all accessible by this method.

^{7}Li-NMR Spectra In Table 4 are listed Lamor frequencies at 21,100 Gauss magnetic field and chemical shifts from LiCl in DMSO-d_6 for some representative ^{7}Li compounds. Generally chemical shifts of ^{7}Li are highly affected by solvation in polar solvents and, at the same time, by states of their aggregation.[13] The ^{7}Li chemical shifts of these compounds are plotted against concentrations in Fig. 1. With each sample tested, lithium nuclei are more shielded at lower concentrations and shielding orders among these samples are not changed. Each chemical shift approaches more closely the values intrinsic to each lithium compound with dilution of samples. These chemical shifts

Table 4 ^{7}Li Chemical shifts from 0.082 M LiCl in DMSO-d_6 and Lamor frequencies for 8 - 11 in ether-hexane(10 : 1)solution.

Compd.	Lamor Frequencies at 21,100 Gauss (34.8 MHz+, KHz)	Chemical shifts from LiCl (ppm)
n-BuLi (8)	23.6806	2.40
PhLi (9)	23.6625	1.88
PhC≡CLi (10)	23.6398	1.23
(1)	23.6269	0.86
$LiClO_4$ (11)	23.5883	-0.25

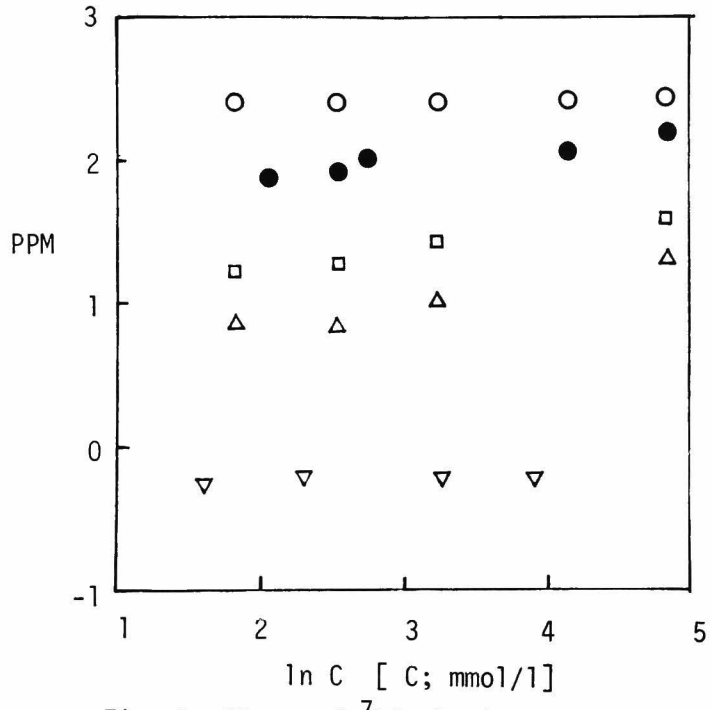


Fig. 1 Plots of ^{7}Li chemical shifts at various concentrations- ○) n-BuLi; ●) PhLi; □) PhC≡CLi; △) 1; ▽) $LiClO_4$.

at high dilution should be the value with least aggregation and sufficient solvation by ether. Therefore following discussion is based on these chemical shift values(Table 4). These chemical shifts are in the range of -0.3 - 2.5 ppm, where the most cationic Li atom (in 11) is most shielded and the reverse is true(in 8). The most shielding for the most cationic Li atom should be atrributable to difusion of the positive charge on Li atoms as a result of the most effective solvation by ether. It is noteworthy that there is considerable correlation between ^{7}Li chemical shifts and hybridization of the α-carbon atoms. The ^{7}Li nuclei are shielded in the order of $sp_3 > sp_2 > sp$. Hybridizations

of the α-carbons are surely correlated with the polarization of Li - C bonds and hence should be correlated with the chemical shifts of ^{7}Li. Effect of ring current on ^{7}Li chemical shifts of 9 seems to be little in comparision with those observed in ^{1}H-NMR spectra of aromatic compounds. Chemical shift of 1 is closest to that of 10. This fact suggests the carbene carbon of 1 is almost sp hybridized on bonding with Li atom. Furthermore the fact that Li nucleus of 1 is 0.37 ppm more shielded than that of 10 indicates more ionicity of the C-Li bond of 1. This finding is also supported from the results of the following Li-Li exchange experiments. At room temperature, rapid Li-Li exchange occurs in a 1 : 1 mixture of n-BuLi and $LiClO_4$, and consequently one signal line is observed in the ^{7}Li-NMR spectrum. This signal line gradually broaden with lowering of temperature and, below -12°C, this signal splits definitely into two peaks. Difference in chemical shift of these two peaks changes no longer below -49.5°C(Fig. 2). Free energy of activation ΔG for Li-Li exchange can be roughly evaluated using formula of Stewart and Siddall.[14] Similarly ΔG for 9 and 10 are also estimable. On the other hand, the signal line for ^{7}Li of 1 never splits into two peaks and only broadening is observed even at -89°C. Therefore ΔG and activation energy E_a are evaluated utilizing the method of Lambert[15] by measuring half line width at variable temperatures. These values are summarized in Table 5 in which k_c is the rate constant for Li-Li exchange at coalescence temperature and k_0 is that at 0°C. ΔG Values decreased in the order of 8, 9, 10, and 1. Even if taking account of aggregation of these compounds at these

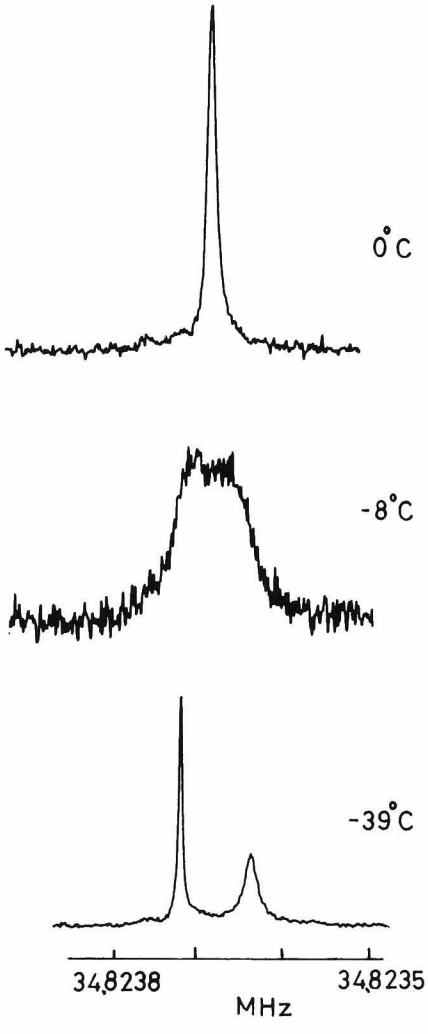


Fig. 2. ^{7}Li Signals on a 1 : 1 mixture of n-BuLi(0.025M) and $LiClO_4$(0.025M) at 0, -8, and -39°C.

Table 5 Kinetic parameters on for Li-Li exchange between 8 - 1 and $LiClO_4$·4.

Compd.	T_c(K)	k_c	k_0	ΔG_c(Kcal/mol)
8	261	3.8×10^2	1.2×10^3	12.1
9	235	1.8×10^2	5.8×10^3	11.2
10	233	2.3×10^2	8.8×10^3	11.0
1	< 184	$< 1.7 \times 10^2$	3.1×10^4	8.7*
				(E_a = 8.6 Kcal/mol, log A = 14.6)

*) Average value between -79 and -89°C.

temperatures, above ΔG values should fairly reflect the degree of ionic character of Li-C bonds of these compounds. In addition, above order of ΔG is in good aggreement with the order of ^{7}Li chemical shifts. These results also indicate appreciable ionic C-Li bonding of 1 mentioned earlier.

From these phenomena, it is concluded that 1 possesses a character considerably close to that of 1-aminocyclopropenyllithium itself.

EXPERIMENTAL

Extended Hückel and MINDO/3 MO Calculations for Cyclopropenylidenes.

Energy levels of wave functions and charge densities on carbene carbons were computed for each cyclopropenylidene using well-established extended Hückel[16] and MINDO/3[17] MO methods. In the extended Hückel MO calculations, the diagonal elements of the Hamiltonian matrix (H_{ij}) were approximated by the atomic valence state ionization potentials(V.S.I.P.). These are summarized in Table 6 with the orbital exponents employed for each element. The C_1-C_2, C_2-C_3, and C_3-C_1 distances are optimized at 1.41, 1.32, and 1.41 Å respectively for each cyclopropenylidene ring. Two substituent groups X are set co-planar with the C_3 ring in xy plane(Fig. 3). As for two methyl groups of bismethylcyclopropenylidene the carbons are sp_3 hybridized and coordinated symmetrically to x axis with each one C-H bond on the two methyl groups lying on xy plane away from xz plane. In bis phenylcyclopropenylidene two phenyl fragments are set co-planer with xy plane and coordinated symmetrically to x axis. In bisthiocyclopropenylidene two mercapto groups are put co-planer with xy plane and coordinated symmetrically to x axis with each hydrogen away from xy plane. In bisaminocyclopropenylidene, two amino groups are co-planer with xy plane and coordinated symmetrically to x axis. The other geometrical parameter were estimated as shown in Table 7.

Table 6 Orbital exponents and V.S.I.P. employed in the present extended Hückel MO calculations.

	H	C		N		S		
	1s	2s	2p	2s	2p	3s	3p	3d
Orbital exponent	1.000	1.625		1.950		1.817		1.000
V.S.I.P. (ev)	-13.16	-21.4	-11.4	-26.0	-13.4	-20.1	-13.3	-2.07

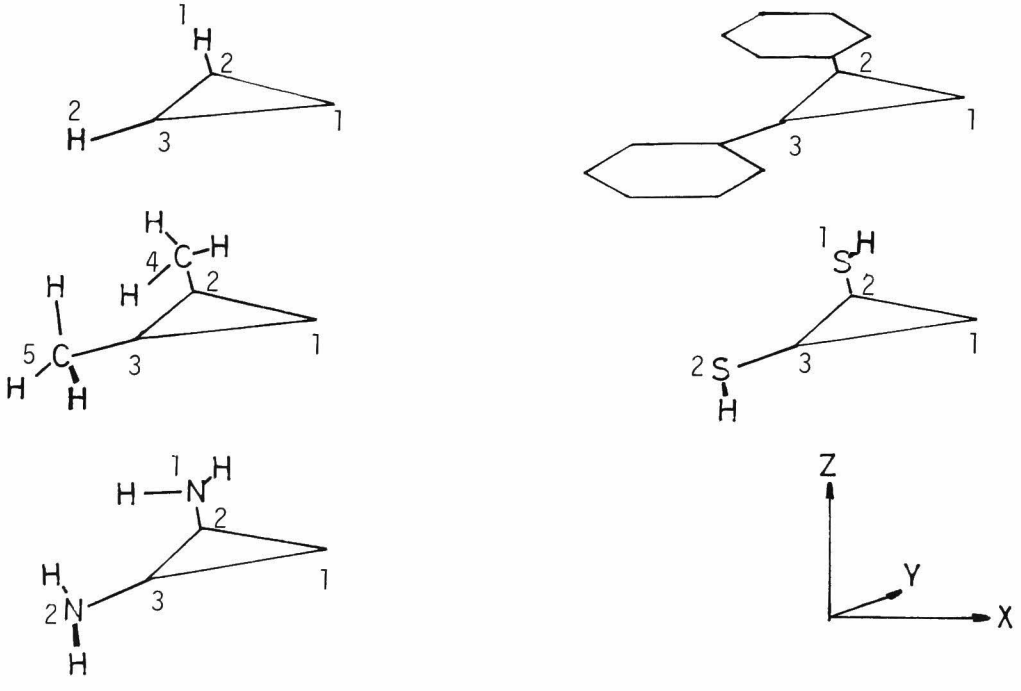


Fig. 3

Table 7 Other geometrical parameters for the present MO calculations.

X	bond distance (Å)	bond angle (deg)
H	H_1-C_2 = H_2-C_3 = 1.070	$H_1C_2C_3$ = $H_2C_3C_2$ = 150
CH_3	C_2-C_4 = C_3-C_5 = 1.460	$C_4C_2C_3$ = $C_5C_3C_2$ = 150
	C-H(Me) = 1.090	HCH(Me) HCC(Me) = 109.5
Ph	C_2-Ph = C_3-Ph = 1.448	PhC_2C_3 = PhC_3C_2 = 150
	C-C(Ph) = 1.397	CCC(Ph) = CCC_2(Ph) = CCC_3(Ph) = 120 HCC(Ph) = 120
SH	C_2-S_1 = C_3-S_2 = 1.730	$S_1C_2C_3$ = $S_2C_3C_2$ = 150
	S-H = 1.381	HSC = 102.5
NH_2	C_2-N_1 = C_3-N_2 = 1.338	$N_1C_2C_3$ = $N_2C_3C_2$ = 150
	N-H = 0.993	HNC = HNH = 120

Preparation of 1[12]. To a solution of 2a(0.816 mmol) in hot dry deoxygenated ether(32 ml) was added 0.64 ml of 15 % n-BuLi in hexane under atmosphere of argon. The pale yellow solution resulted was 0.025 M with 1. This solution was used in the following experiments.

Reaction of 1 with AcOD. To an ethereal solution(10 ml) of 1 was added 1 ml of AcOD. After stirring for 5 min, resulting suspension was evaporated to dryness and extracted with 30 ml of methylene chloride. Solvent was removed and the residue was crystallized from methylene chloride / ether, giving colorless crystals of 2b in 98 % yield: mp. 203°C; IR(KBr): 2980, 2380, 1880, 1571, 1350, 1096, 621 cm^{-1}; PMR($CDCl_3$): δ 3.95, 3.87 (m, CH_3), 1.40 ppm (d, CH_3).

Reaction of 1 with methallyl chloride. To a cool(-78°C) ethereal solution(32 ml) of 1 was added methallyl chloride(0.85 mmol). After Stirring overnight 1 ml of 5% aq. $HClO_4$ was added. Organic layer was extracted with methylene chloride, washed with water, dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel with ethyl acetate/acetone(6/1). To this was added 100 mg of sodium tetraphenylborate and stirred for 2h. After usual work-up, this was crystallized from methanol/ether to afford pale yellow crystals of 2d in 56 % yield: mp. 133°C; IR(KBr): 3045, 2980, 1904, 1545, 1476, 1450, 1344, 1135, 730, 600 cm^{-1}; PMR($CDCl_3$): δ 5.01, 4.72(br, $=CH_2$), 4.01, 3.94(sep, CH), 3.48(br, CH_2), 1.84(s, CH_3), 1.37 ppm(d, CH_3).

Anal. calcd for $C_{43}H_{55}BN_2$: C, 84.57; H, 9.08; N, 4.59.

Found : C, 84.26; H, 9.29; N, 4.48.

Reaction of 1 with acetic anhydride. To an ethereal solution(10 ml) of acetic anhydride(0.85 mmol) was added dropwise an ethereal solution(32 ml) of 1 at -78°C. After 30 min the mixture was warmed up to room temperature and then added 1 ml of 5 % aq. $HClO_4$. The organic layer was extracted with 50 ml of methylene chloride and washed with water. After drying($MgSO_4$) and evaporation of the solvent, the residue was chromatographed on silica gel with methylene chloride/acetone, affording colorless crystals of 2f in 65 % yield: mp. 145°C; IR(KBr): 2980, 1860, 1670, 1580, 1459, 1374, 1353, 1149 1090, 1023, 965, 710 cm^{-1}; PMR($CDCl_3$): δ 4.18, 4.07(m, CH), 2.67(s, $COCH_3$), 1.48, 1.45 ppm(d, CH_3); ^{13}C NMR($CDCl_3$): δ 183.3(CO), 130.8(C_{ring}-N), 102.0(C_{ring}-Ac), 55.7, 51.2(CH), 31.3($CO\underline{C}H_3$), 20.7 ppm(CH_3).

Anal. calcd for $C_{17}H_{31}ClN_2O_5$: C, 53.81; H, 8.50; N, 7.55.

Found : C, 53.89; H, 8.25; N, 7.39.

Reaction of 1 with ethyl chlorocarbonate. Similarly 2g was obtained from ethyl chlorocarbonate(0.8 mmol) and equimolar amounts of 1. Crystallization from methylene chloride/ether gave colorless crystals in 68 % yield: mp. 136°C; IR(KBr): 2980, 1895, 1723, 1598, 1463, 1399, 1379, 1355, 1227, 1205, 1176, 1153, 1090, 1010, 753, 620 cm^{-1}; PMR ($CDCl_3$): δ 4.43(q, CH_2), 4.23, 4.05(sep, CH), 1.51, 1.46(d, CH_3), 1.40 ppm(t, CH_3).

Anal. calcd for $C_{18}H_{33}ClN_2O_6$: C, 52.87; H, 8.13; Cl, 8.67; N, 6.85.

Found : C, 52.63; H, 8.21; Cl, 8.85; N, 6.77.

Similar procedure gave 2h from ethyl chlorocarbonate(0.4 mmol) and twice molar amounts of 1. Crystallization from methanol / ether afforded pale yellow crystals in 31 % yield: mp. 146°C(dec.); IR(KBr): 2980, 1897, 1698, 1583, 1540, 1466, 1351, 1253, 1090 cm^{-1}; PMR($CDCl_3$): δ 4.50 - 3.10(m, CH, CH_2), 1.60 - 0.80 ppm(m, CH_3).

Anal. calcd for $C_{33}H_{63}ClN_4O_6$: C, 61.23; H, 9.81; Cl, 5.48; N, 8.58.

Found : C, 61.27; H, 9.86; Cl, 5.52; N, 8.65.

Reaction of 1 with CO_2. An ethereal solution(32 ml) of 1 was poured onto dry-ice under atmosphere of argon. After warming up to room temperature the solvent was evaporated to dryness, which gave 2i as yellow solid, fairly hygroscopic: IR(KBr): 2980, 1920, 1895, 1630, 1557, 1440, 1346, 1304, 1180, 1140, 1114, 1082, 896, 854, 823 cm^{-1}; PMR($CDCl_3$): δ 4.00(br, CH), 1.40 ppm(m, CH_3).

Anal. calcd for $C_{16}H_{30}ClLiN_2O_6 \cdot 2H_2O$: C,45.45; H,7.63; Cl,8.38; N,6.63.

Found : C,45.07, H,7.35; Cl,7.92; N,6.52.

Decarboxylation of 2g and 2i. Suspension of 2g in 0.4 % aq. K_2CO_3 (20 ml) was stirred for a day. After neutralization with 0.1 % aq. $HClO_4$, the mixture was extracted with methylene chloride, dried(Na_2SO_4) and evaporated. There was obtained quantitative yields of 2a as colorless crystals..... Suspension of 2g in a mixture of methylene chloride and 70 % aq. $HClO_4$(10 ml) was stirred for 3h. After usual work-up, almost pure 2a was obtained.....

Decarboxylation of 2i easily proceeded in the presence of a small amount of water or acid to afford 2a almost quantitatively.

Reaction of 1 with CS_2. To an ethereal solution(32 ml) of 1 was added CS_2(2 ml) at -78°C. After stirring for 0.5 h at room temperature, this was evaporated to dryness. Chromatography on silica gel with methylene chloride/ethyl acetate(3/1) and crystallization from methylene chloride/ether afforded red crystals of 2j in 27 % yield: mp. 218°C (dec.);IR(KBr): 2980, 1900, 1530, 1445, 1214, 1182, 1156, 1140, 1044, 1036, 959 cm^{-1}; PMR($CDCl_3$): δ 3.85 (m, CH), 1.41 ppm(d,CH_3); UV(CH_3CN): $\lambda_{max}(\varepsilon_{max})$ 223(26600), 274(sh, 7910), 357(14900), 514 nm(185).

Anal. calcd for $C_{16}H_{28}N_2S_2$: C, 61.49; H, 9.03; N, 8.96; S, 20.52.

found : C, 61.71; H, 9.26; N, 8.97; S, 20.35.

Reaction of 1 with benzoquinone. Similarly 2k was obtained from benzoquinone(0.8 mmol) and an equimolar amount of 1. Chromatography on silica gel with benzene/acetone(1/1) gave white crystals in 47 % yield : mp. 210°C(dec.); IR(KBr): 3410, 2980, 1919, 1557, 1494, 1373, 1341, 1209, 1100, 925, 822, 782 cm^{-1}; PMR(DMSO-d_6): δ 9.59, 9.24, 6.83, 6.65

(m, Ph), 3.99(sep, CH), 3.32(s, OH), 1.34, 1.29 ppm(d, CH_3); ^{13}C NMR(DMSO-d_6): δ 134.2(C_{ring}-N), 106.3(C_{ring}-Ar), 149.9, 147.4, 118.9, 117.0, 114.8, 112.5 ppm(Ar).

Anal. calcd for $C_{21}H_{33}ClN_2O_6$: C, 56.69; H, 7.48; N, 6.30.

Found : C, 56.64; H, 7.48, N, 6.09.

Reaction of 1 with BF_3/ether. To a solution(32 ml) of 1 was added BF_3/ether(0.8 mmol) at 0°C. After stirring for 3h, was added 50 ml of methylene chloride to the mixture, washed several times with water, dried($MgSO_4$) and the solvent was evaporated. The residue was chromatographed on silica gel with benzene/methylene chloride(1/1). Crystallization from methylene chloride/ether gave colorless crystals of 3 in 78 % yield: mp. 211°C; IR(KBr): 2980, 1873, 1513, 1345, 1028, 1018, 937 cm^{-1}; PMR($CDCl_3$): δ 3.93(sep, CH), 1.38 ppm(d, CH_3).

Anal. calcd for $C_{15}H_{28}BF_3$: C, 59.23; H, 9.28; N, 9.21.

Found : C, 59.11; H, 9.18; N, 9.10.

Reaction of 1 with Pd, Pt, and Rh complexes. These will be described in detail in Chapter 2.

Reaction of 1 with Ti complex. To $(\pi\text{-}C_5H_5)_2TiCl_2$(0.625 mmol) in 50 ml of ether was added an ethereal solution(25 ml) of 1. After stirring for 2h, this was poured into 5 % aq. $HClO_4$, washed several times with water, dried and evaporated. The residue was chromatographed on silica gel with methylene chloride/ether to afford red crystals of 6 in 34 % yield: mp. 175°C(dec.); IR(KBr): 3099, 2980, 1841, 1473, 1452, 1373, 1210, 1100, 1017, 817, 701, 623 cm^{-1}; PMR($CDCl_3$): δ 6.30, 6.22(s, C_5H_5)

, 4.20(sep, CH), 1.50 ppm(d, CH_3).

Anal. calcd for $C_{25}H_{38}Cl_2N_2O_4Ti$: C, 55.66; H, 6.97; N, 5.10.

Found : C, 55.42; H, 6.85; N, 5.17.

Reaction of 1 with $AgSO_3CF_3$. To $AgSO_3CF_3$(0.55 mmol) in ether(20 ml) was added an ethereal solution(44 ml) of 1, avoiding sun light. The reaction mixture was poured into 100 ml of 1 % aq. $HClO_4$ and extracted with 50 ml of methylene chloride. After washing, drying($MgSO_4$) and evaporation, recrystallization from methylene chloride/ether afforded slightly grayish crystals of 7 in 67 % yield: mp. 165°C(dec.); IR(KBr): 2980, 1845, 1501, 1338, 1273, 1135, 1090, 1031, 1018, 636, 620, 545 cm^{-1}; PMR($CDCl_3$): δ 3.87(sep, CH), 1.43 ppm(d, CH_3): ^{13}C NMR ($CDCl_3$): δ 149.5(C_{ring}-N), 137.2(br, C_{ring}-Ag), 56.2, 48.7(CH), 21.4 ppm(br, CH_3).

Anal. calcd for $C_{30}H_{56}AgClN_4O_4$: C, 52.98; H, 8.30; N, 8.24.

Found : C, 52.62; H, 8.37; N, 8.11.

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CHAPTER 2

SYNTHESES AND PROPERTIES OF BISAMINOCYCLOPROPENYLIDENE (Pd, Pt, Rh) COMPLEXES

SUMMARY

The transition metal complexes of bisaminocyclopropenylidene, trans-X_2-μ-$X_2M[C_3(NR_2)_2]$ [1: R_2N= Me_2N, Et_2N, $(i\text{-}Pr)_2N$, t-BuN$(CH_2)_3$N(t-Bu); X= Cl, I; M= Pd, Pt], cis-$MX_2[C_3(NR_2)_2]L$ [2: R_2N= Me_2N, Et_2N, $(i\text{-}Pr)_2N$, t-BuN$(CH_2)_3$N(t-Bu); X= Cl; M= Pd, Pt; L= PR'_3, py], and trans-$ML'[C_3(NR_2)_2]L_2\cdot ClO_4$ [3: R_2N= Me_2N, Et_2N, $(i\text{-}Pr)_2N$, t-BuN$(CH_2)_3$N(t-Bu); L'= Cl, CO; M= Pd, Pt, Rh; L= PR'_3], were synthesized by oxidative addition of cyclopropenium cations $(R_2N)_2C_3X\cdot X$ to zero valent metals, nucleophilic cleavage of halogen-bridge, ligand exchange, and the direct metal exchange reaction between cyclopropenylidene lithium $(i\text{-}Pr_2N)_2C_3Li\cdot ClO_4$ and trans-$XML'L_2$.

INTRODUCTION

As was observed and discussed in Chapter 1, bisaminocyclopropenylidene lithium has the character close to bisaminocyclopropenylidene itself. However this species is not so stable as to be isolable. Transition metal complexes of bisaminocyclopropenylidenes would be more stable. The studies about these transition metal complexes may provide valuable information regarding structures of bisaminocyclopropenylidenes. In addition it seems important to clarify the properties of bisaminocyclopropenylidene as a organic ligand from the standpoint of organometallic chemistry.

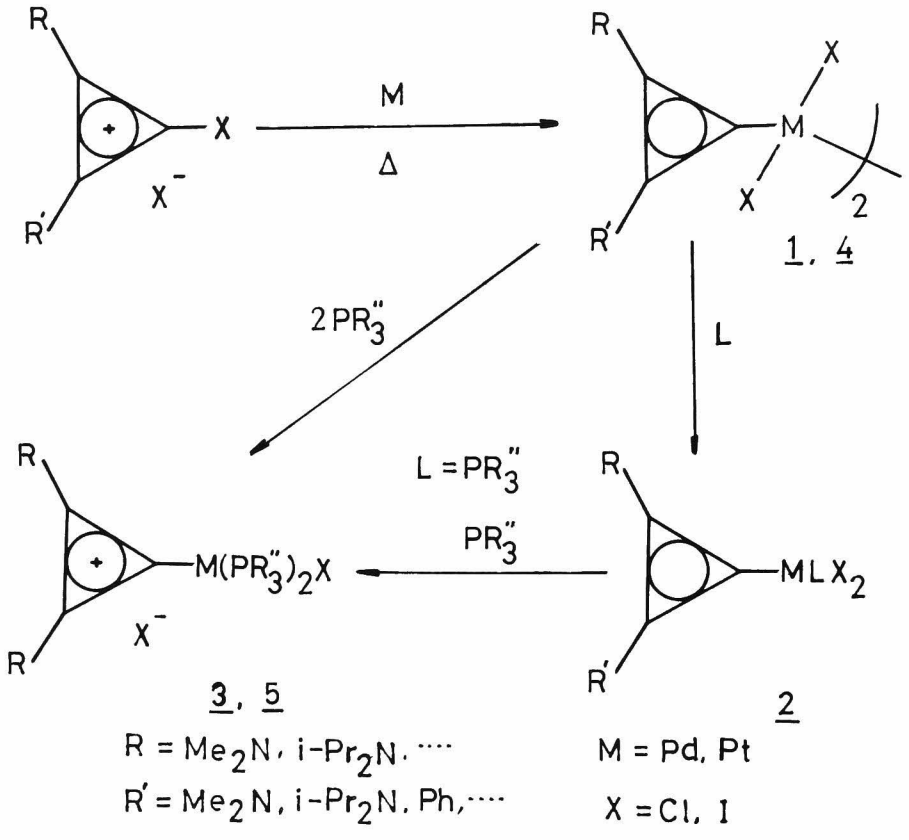
In this chapter, I wish to describe about the syntheses and properties of several bisaminocyclopropenylidene (Pd, Pt, Rh) complexes.

RESULT AND DISCUSSION

Synthesis. Two types of synthetic methods have been found for bisaminocyclopropenylidene Pd^{II} complexes. The first, (A) contains oxidative addition of bisamino-halocyclopropenium halides to zerovalent metals. The second, (B) involves nucleophilic attack of lithiocyclopropenylidenes on suitable transition metal complexes.

Bisamino-halocyclopropenium halides react with Pd and Pt black in refluxing acetonitrile to afford halogen-bridged binuclear complexes 1. For instance, a mixture of 1,2-bis(di-i-propylamino)-3-chlorocyclopropenium chloride and slightly excess amounts of palladium black in acetonitrile was heated under reflux for 6 h. Chromatography on silica gel with methylene chloride/ether (1:1) followed by recrystallization from the same solvent afforded reddish orange crystals of 1a in 44 %

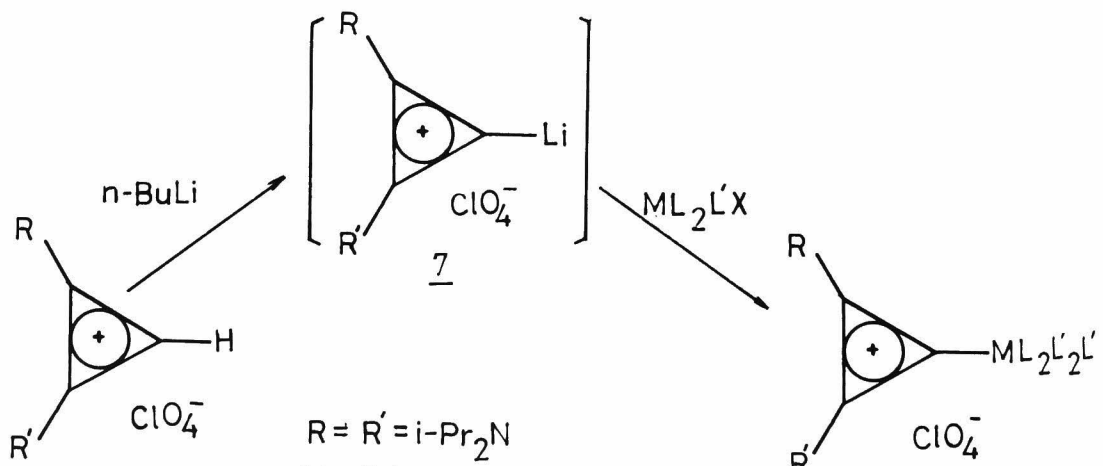
(A)



R = Me_2N, i-Pr_2N, ····
R' = Me_2N, i-Pr_2N, Ph, ····

M = Pd, Pt
X = Cl, I

(B)



R = R' = i-Pr_2N
M = Pd, Pt, Rh
L = n-Bu_3P
L' = Cl, CO
X = Cl

Table 1 Yields and properties of bisaminocyclopropenylidene transition metal complexes 1 - 5.

	R_2N	R_2N	M	X	L	Yield(%)	M.p.(°C)	Color
1a	Me_2N	Me_2N	Pd	Cl		44[a]	210(dec.)	reddish orange
1b	Et_2N	Et_2N	Pd	Cl		75[a]	213(dec.)	reddish orange
1c	i-Pr_2N	i-Pr_2N	Pd	Cl		44[a]	240(dec.)	reddish orange
1d	-N(t-Bu)$(CH_2)_3$(t-Bu)N-		Pd	Cl		87[a]	223(dec.)	reddish orange
1e	i-Pr_2N	i-Pr_2N	Pt	I		18[a]	226(dec.)	orange
2a	Me_2N	Me_2N	Pd	Cl	n-Bu_3P	85[b]	172	white
2b	Et_2N	Et_2N	Pd	Cl	n-Bu_3P	82[b]	142	white
2c	i-Pr_2N	i-Pr_2N	Pd	Cl	n-Bu_3P	78[b]	208	white
2d	i-Pr_2N	i-Pr_2N	Pd	Cl	Ph_3P	87[b]	260(dec.)	pale yellow
2e	-N(t-Bu)$(CH_2)_3$(t-Bu)N-		Pd	Cl	n-Bu_3P	86[b]	218	white
2f	Me_2N	Me_2N	Pd	Cl	C_5H_5N	88[b]	151(dec.)	yellow

Table 1 Continued

	R_2N	R_2N	M	X	L	Yield(%)	M.p.(°C)	Color
3a	Me_2N	Me_2N	Pd	Cl	n-Bu_3P	71[b]	129	white
3b	Me_2N	Me_2N	Pd	Cl	Ph_3P	95[b]	240(dec.)	pale yellow
3c	Et_2N	Et_2N	Pd	Cl	n-Bu_3P	89[b]	78	white
3d	i-Pr_2N	i-Pr_2N	Pd	Cl	n-Bu_3P	67[c]	120	white
3e	-N(t-Bu)$(CH_2)_3$(t-Bu)N-		Pd	Cl	n-Bu_3P	94[b]	137	white
3f	i-Pr_2N	i-Pr_2N	Pt	Cl	n-Bu_3P	58[c]	154	pale yellow
3g	i-Pr_2N	i-Pr_2N	Rh	CO	n-Bu_3P	43[c]	195	yellow
4	i-Pr_2N	Ph	Pd	Cl		44[d]	206(dec.)	reddish orange
5	i-Pr_2N	Ph	Pd	Cl	Ph_3P	58[e]	207(dec.)	pale yellow

a) Yield from bis(amino)halocyclopropenium halide. b) Yield from 1. c) Yield from 6c. d) Yield from amino-phenyl-halocyclopropenium halide. e) Yield from 4.

yield. Similarly palladium and platinum complexes 1b-e were synthesized.

The halogen bridge on 1 is easily cleaved in the presence of phosphine to give mononuclear complexes 2. Analogously, Pd complexes of amino-phenylcyclopropenylidene 4 and 5 can be obtained. Further ligand exchange is possible for 2 in the presence of excess amounts of the phosphine, so that cationic complexes 3 are obtainable.

The cationic complexes can also be synthesized even more easily as follows. Bisaminocyclopropenium perchlorate 6c was treated with n-BuLi to afford bisaminocyclopropenylidene lithium 7, which reacts easily with transition metal complexes such as $ML_2L'Cl$ to give Pd and Pt complexes 3. This is also an effective way to synthesize the cationic Rh^I complexes of bisaminocyclopropenylidenes. These complexes in Table 1 are very stable in the air at room temperature. For example ir spectra and melting points of 3g never changed after several months. Moreover 2a was not hydrolyzed by treatment with 5 % $HClO_4$ and 3 N KOH aq.

Ligand Co-ordination. Information about configuration of the complexes 1 - 3 can be obtained from far infrared spectra. The complex 1a exhibits three absorption bands due to stretching vibrations of three different pairs of Pd-Cl bonds in 260 - 340 cm^{-1}. This absorption pattern is characteristic of the μ-chloro binuclear type complexes.[1] The Pd-Cl stretching absorption bands of complexes of carbenes, $LPd(PR_3)Cl_2$, have been well studied.[2] These complexes exhibit one or two absorption bands at 330 - 360 cm^{-1} when they are the trans isomers and at 270 320 cm^{-1} when they are the cis isomers. Therefore monomeric

Table 2 Pd - Cl stretching absorption bands on the complexes 1, 2, and 3.

	ν_{Pd-Cl} (cm^{-1})		
1a	344,	290,	272
1b	342,	291,	280
1c	340,	285,	262
2a	292,	269	
2b	304,	282	
2c	304,	286	
2d	304,	286	
3a	295		
3f	300		

complexes 2 listed in Table 2 should be cis isomers. Additional support for this is obtained from their ^{13}C-NMR spectra. Coupling constants $^{2}J(C_{carbene}\text{-Pd-P})$ of 2 shown in Table 3 are all too small to be ascribed to the trans isomers.[3] The cationic complexes 3 prepared from 2 have the same configuration as that of those prepared from 7 and trans-$ML_2L'Cl$. . In ^{13}C-NMR spectra, signals for each carbene carbon of 3 appear as a triplet due to equal coupling of the carbene carbons with two phosphorous nuclei. These indicate all cationic complexes 3 in Table 3 to be trans isomers.

It is well known that Pd complexes such as cis-L_2PtCl_2(L= PR_3,---) isomerize to trans isomers in refluxing ethanol. However, no isomerization was detected for 2b even after 8 h in refluxing ethanol. Thermodynamic stability of the cis-isomers of the cyclopropenylidene palladium complexes should be similar to that of Wanzlic type carbene complexes.

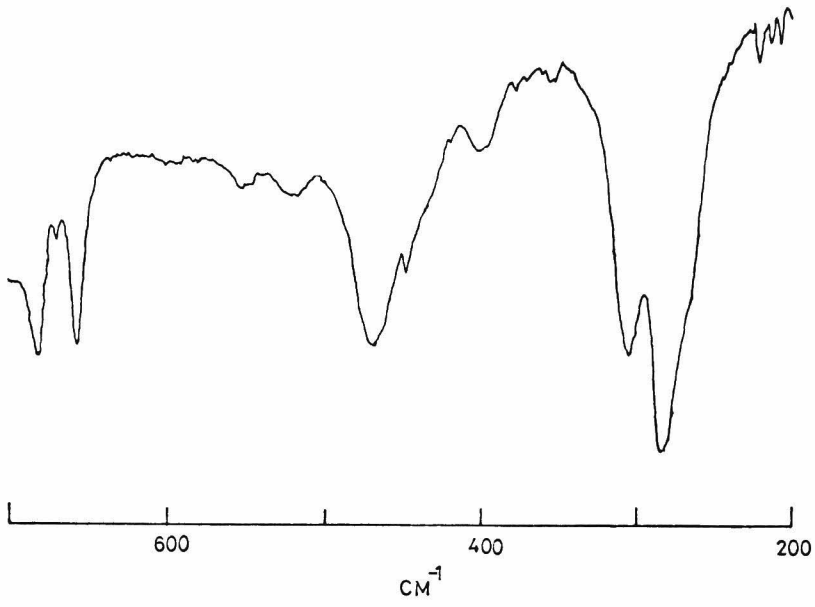


Fig. 1. Far-infrared spectrum of 2b (CeI).

Table 3 ^{13}C-Chemical shifts and coupling constants of C-3 ring carbons on the complexes, 1, 2, 3.

Compd.	$\delta(C_{ring}\text{-}R)$	$\delta(C_{ring}\text{-}M)$		$^2J_{C_{ring}\text{-}P}$(Hz)	Solv.
1a	150.9	99.9			CD_2Cl_2
1c	148.3	106.5			$CDCl_3$
4	136.9,130.3	133.4			CD_2Cl_2
2a	150.6	125.0	d	6.1	$CDCl_3$
2b	149.5	125.6	d	5.9	$CDCl_3$
2c	147.4	128.4	d	4.9	$CDCl_3$
2e	150.5	122.7	d	3.7	CD_2Cl_2
3a	151.6	122.0	t	10.5	$CDCl_3$
3d	147.8	125.6	t	11.3	$CDCl_3$
3g	149.9	147.8	pair* of t	18.3	$CDCl_3$

*) $J_{C_{ring}\text{-}Rh}$ = 43.0 Hz.

The Bisaminocyclopropenylidene Ligands. In ^{13}C-NMR spectra signals for the ring carbons of 1a - 4 appear at two positions in the region of 99.9 - 151.6 ppm (Table 3). For instance carbene carbon of 2a appears as a doublet at 120.5 ppm and the other two ring carbons as a singlet at 150.6 ppm (Fig. 2). On the other hand signals for the carbene carbon of 3g appear as a pair of triplets at 147.8 ppm and those for the carbonyl carbon are observed also as a pair of triplets at 192.2 ppm (Fig. 3).

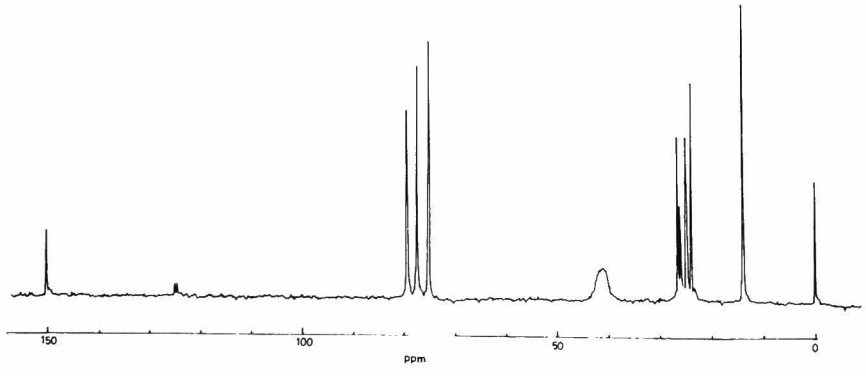


Fig. 2. ^{13}C-NMR spectrum of 2a.

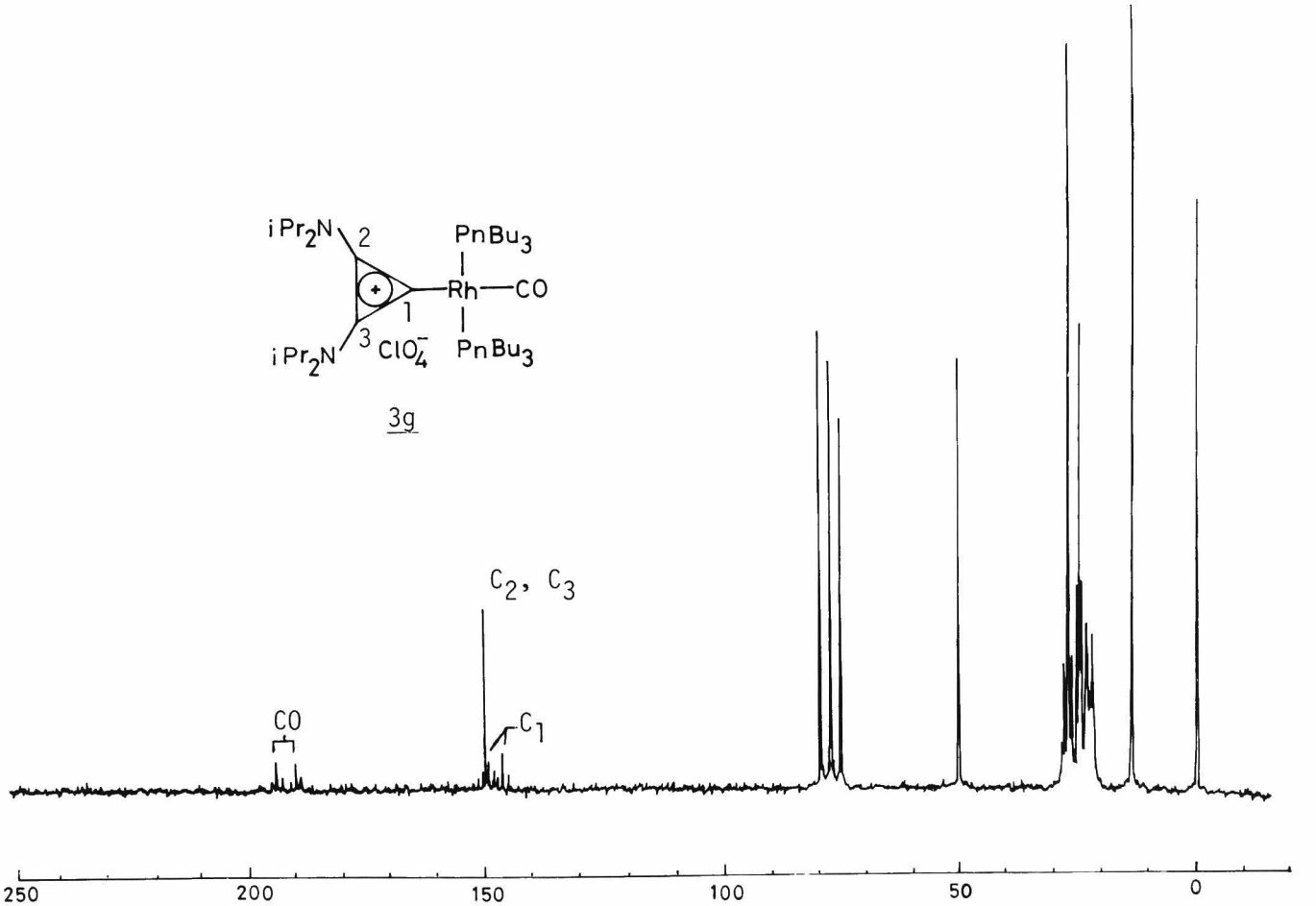


Fig. 3. ^{13}C-NMR spectra of 3g.

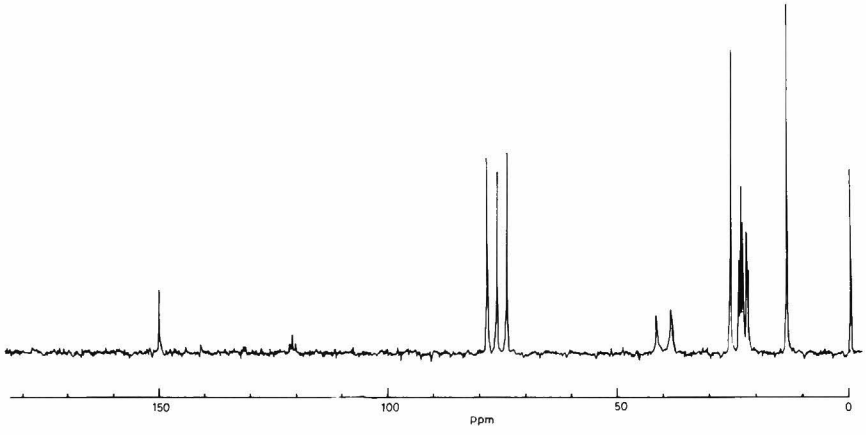


Fig. 4. ^{13}C-NMR spectrum of 3a.

Every infrared spectrum of bisaminocyclopropenylidene complexes 1a - 3g shows two strong characteristic bands. One is in the region of 1854 - 1903 cm^{-1} and the other is in the region of 1485 - 1570 cm^{-1}. The former is assigned to the ring deformation and the latter is the stretching vibrational bands for the C_{ring}-N bonds. These data for the representative complexes are shown in Table 4.

Every absorption band of the complexes 1a - 3g occur at lower frequencies in comparison with that of corresponding bisaminocyclopropenium cations 6a - d. The lower shifts of the latter bands should be attributed to the relaxation of C_{ring}-N bond, namely to the decreasing of π-orbital interaction between nitrogen lone pair and C-3 ring π system. These **trends** in infrared spectra are consistent with the following observation with free energy of activation to rotation about C_{ring}-N

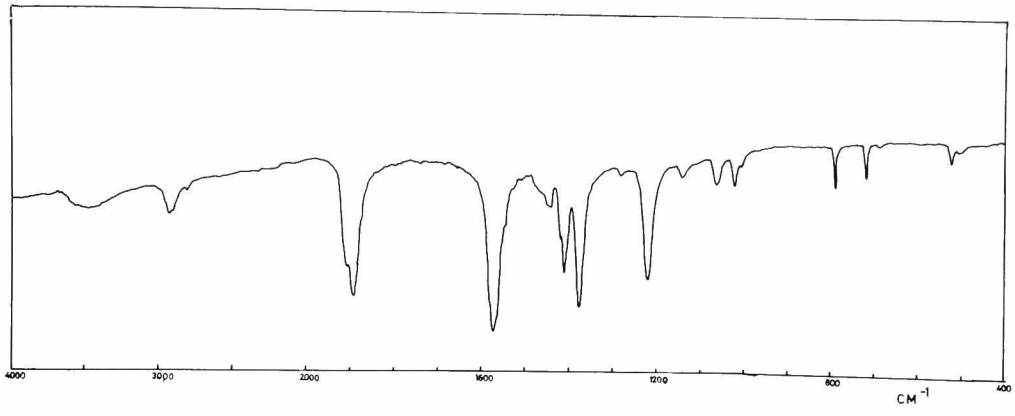


Fig. 5. Infrared spectrum of 1a.

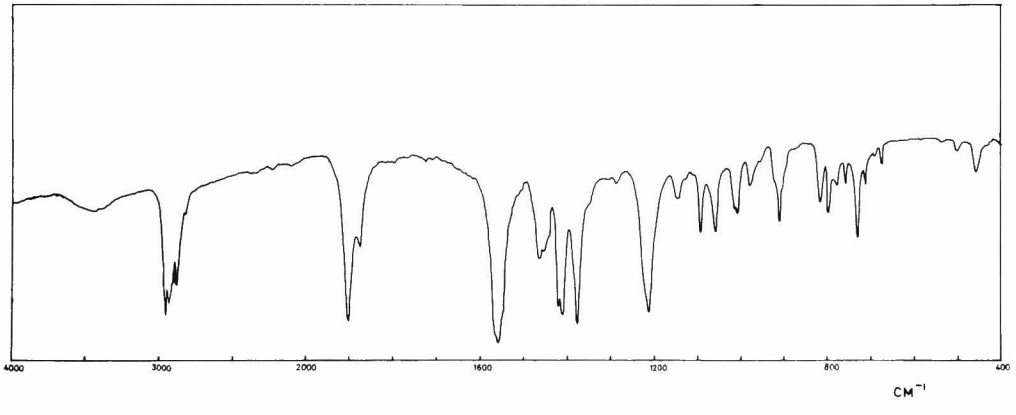


Fig. 6. Infrared spectrum 2a.

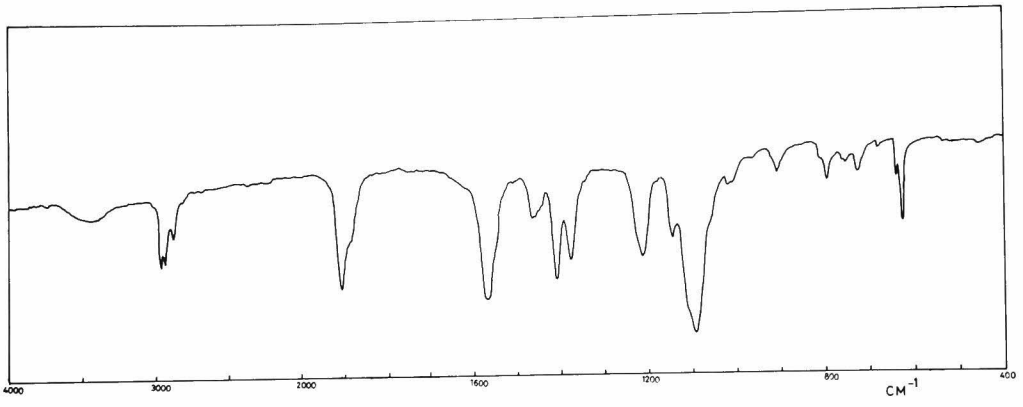


Fig. 7. Infrared spectrum of 3a.

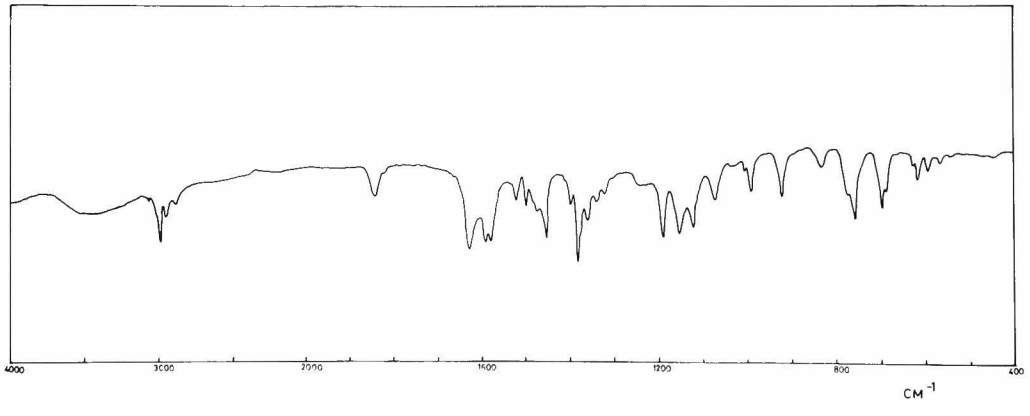


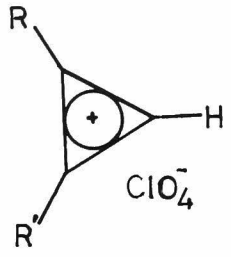
Fig. 8. Infrared spectrum of 4.

Table 4 The ring deformation and C_{ring}-N streching absorption bands, and ΔG_c to rotation about the C_{ring}-N bonds on 1a-3g and 6a.

	ν_Δ (cm^{-1})	ν_{C-N}	ΔG_c (Kcal/mol)
1a	1890	1570	15.6
1b	1888	1551	15.4
2a	1903	1557	15.4
2b	1886	1526	15.5
2c	1860	1490	≦8.4
2e	1880	1530	
3a	1903	1567	
3c	1886	1523	
3d	1854	1494	≦9.7
3f	1860	1497	
3g	1858	1485	
6a	1915	1616	19.1
6b	1091	1591	
6c	1884	1572	17.8
6d	1908	1610	

bond. In the ^{13}C-NMR spectrum of 2a at 30°C, methyl carbons of the amino groups appear as a single line at 41.2 ppm, and at low temperatures this signal splits into two lines. Free energy of activation to rotation at coalesence temperature (ΔG_c) can be evaluated utilizing the formula of Stewart and Siddall.[5] In 1a - 3d, ΔG_c becomes fairly small in comparison with that of corresponding cyclopropenium cations 6a - c (Table 4).

For the cyclopropenylidene ligands in which the peripheral alkylamino moieties are bulky ones, this trend becomes more pronounced.



R	R'	
Me_2N	Me_2N	6a
Et_2N	Et_2N	6b
i-Pr_2N	i-Pr_2N	6c
-N(t-Bu)-$(CH_2)_3$-N(t-Bu)-		6d

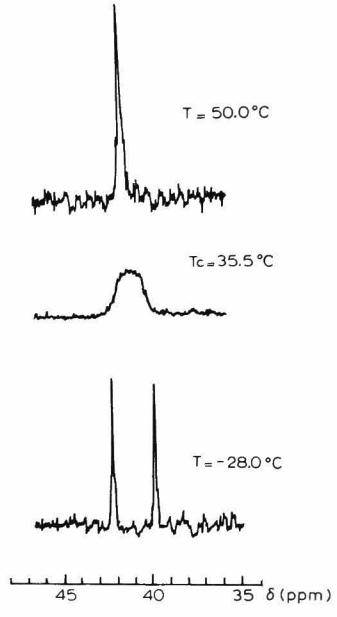
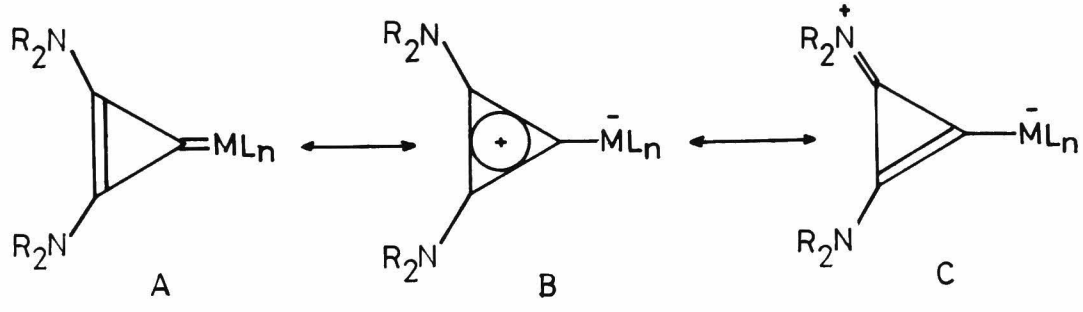


Fig. 9. ^{13}C chemical shift data for the NMe_2 groups of *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$ in CD_2Cl_2.

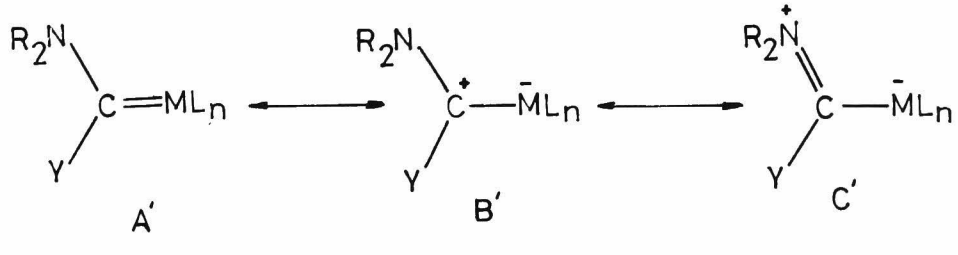
For example ΔG_c of 2c and 3d are less than 9.7 Kcal/mol while that of 6c is 17.8 Kcal/mol. In the infrared spectra, C_{ring}-N stretching bands of 2c, e and 3d, e appear at still lower frequencies than that of 2a, b and 3a, c. Moreover, difference in frequencies between 2c, e and 6c, d is clearly larger than that between 2a, b and 6a, b. Presumably nonbonding interactions between bulky alkylamino groups or between these groups and metal ligands destroy the C_{ring}-N planarity and

induce more decreased multiple bonding character of the C_{ring}-N bond. In spite of these spectroscopic observations the stability of bis(di-i-propylamino)cyclopropenylidene complexes is compared favorably with that of the other bisaminocyclipropenylidene complexes. Bulkiness of this substituent may affect advantageously the stabilization of the complexes.

Following canonical forms can be written to present formal bondings in bisaminocyclopropenylidene complexes:



Decreased multiple bonding character of C_{ring}-N bond generally observed for bisaminocyclopropenylidene palladium complexes suggests that participation of metal d orbital in the π-back bonding from central metal atom to the C-3 ring system (form A) is comparable in its magnitude to that of amino groups (form C). This is interesting in view of the generally accepted dominant contribution of form C' for Wanzlic type carbene complexes.[6)]



EXPERIMENTAL

Trans-X_2-μ-X_2Pd(C_3RR')$_2$(1a - e, 4). A mixture of amino(halo)cyclopropenium halide(1 mmol) and palladium black(1.2 mmol) in freshly distilled acetonitrile (20 ml) was heated for 16 h under reflux.

Trans-Cl_2-μ-Cl_2Pd[$C_3(Me_2N)_2$](1a) - Crystallization from methylene chloride/ether gave reddish orange crystals of 1a in 44 % yield: mp. 210°C(dec.); IR(KBr): 2930, 1890, 1570, 1409, 1375, 1216 cm^{-1}; PMR($CDCl_3$): δ 3.09, 3.32 ppm(s, CH_3); ^{13}C NMR(CD_2Cl_2): δ 150.9(C_{ring}-N), 99.9 (C_{ring}-Pd), 41.3, 42.2 ppm(br CH_3); UV(CH_2Cl_2): λ_{max}(ε_{max}) 366(3080), 306 nm(sh, 1000).

Anal. calcd for $C_{14}H_{24}Cl_4N_4Pd_2$: C, 27.89; H, 4.01; Cl, 23.52; N, 9.29.
Found : C, 28.03; H, 4.28; Cl; 23.57; N, 9.26.

Trans-Cl_2-μ-Cl_2Pd[$C_3(Et_2N)_2$](1b) - Crystallization from methylene chloride/ether afforded reddish orange crystals of 1b in 75 % yield: mp. 213°C(dec.); IR(KBr): 2980, 1888, 1551, 1461, 1438, 1394, 1299, 1181, 1073 cm^{-1}; PMR($CDCl_3$): δ 3.54(m, CH_2), 1.32 ppm(t, CH_3); ^{13}C NMR(CD_2Cl_2): δ 149.9(C_{ring}-N), 100.1(C_{ring}-Pd), 41.7, 46.2(br, CH_2), 14.1 ppm(CH_3).

Anal. calcd for $C_{22}H_{40}Cl_4N_4Pd_2$: C, 36.95; H, 5.64; Cl, 19.83; N, 7.83.
Found : C, 36.92; H, 5.85; Cl, 19.86; N, 7.86.

Trans-Cl_2-μ-Cl_2Pd[$C_3(i\text{-}Pr_2N)_2$](1c) - Crystallization from methylene chloride/ether afforded reddish orange crystals of 1c in 44 % yield : mp. 240°C(dec.); IR(KBr): 2980, 1859, 1500, 1458, 1402, 1373, 1338, 1209, 1176, 1158, 1131 cm^{-1}; PMR($CDCl_3$): δ 3.84(m, CH), 1.52 ppm(m, CH_3); ^{13}C NMR($CDCl_3$): δ 148.3(C_{ring}-N), 106.5(C_{ring}-Pd), 51.5(CH), 21.9

ppm(CH_3); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 327(4460), 373 nm(521).

Anal. calcd for $C_{30}H_{56}Cl_4N_4Pd_2$: C, 43.55; H, 6.82; Cl, 17.14; N, 6.77.
Found : C, 43.78; H, 6.81; Cl, 17.15; N, 6.99.

Trans-Cl_2-μ-Cl_2Pd[$\overline{C_3\text{-}N(t\text{-}Bu)CH_2CH_2CH_2(t\text{-}Bu)N}$](1d) - Crystallization from methylene chloride/ether gave reddish orange crystals of 1d in 87 % yield: mp. 223°C(dec.); IR(KBr): 2978, 1881, 1541, 1341, 1311, 1278, 1210 cm^{-1}; PMR($CDCl_3$): δ 3.43(t, NCH_2), 1.80(m, CH_2), 1.59 ppm(s, CH_3); ^{13}C NMR($CDCl_3$): δ 147.8(C_{ring}-N), 110.2(C_{ring}-Pd), 58.7($\underline{C}CH_3$), 50.2(NCH_2), 30.8(CH_2), 28.5 ppm(CH_3).

Anal. calcd for $C_{28}H_{48}Cl_4N_4Pd_2$: C, 42.29; H, 6.08; Cl, 17.83; N, 7.04.
Found : C, 42.21; H, 6.83; Cl, 18.11; N, 7.04.

Trans-I_2-μ-I_2Pt[$C_3(i\text{-}Pr_2N)_2$](1e) - Crystallization from methylene chloride/ether gave orange crystals of 1e in 18 % yield: mp. 226°C(dec.); IR(KBr): 2980, 1846, 1480, 1459, 1400, 1371, 1336, 1210, 1181, 1162, 1137 cm^{-1}; PMR($CDCl_3$): δ 3.81(m, CH), 1.51 ppm(d, CH_3); ^{13}C NMR($CDCl_3$): δ 106.7(C_{ring}-N), 51.2(CH), 23.0 ppm(CH_3).

Anal. calcd for $C_{30}H_{56}I_4N_4Pt_2$: C, 26.29; H, 4.12; I, 37.04; N, 4.09.
Found : C, 26.30; H, 4.35; I, 37.32; N, 3.92.

Trans-Cl_2-μ-Cl_2Pd[$C_3(i\text{-}Pr_2N)Ph$](4) Crystallization from acetonitryl afforded reddish orange crystals of 4 in 44 % yield: mp. 206(dec.); IR(KBr): 3075, 2980, 1840, 1520, 1480, 1451, 1395, 1360, 1330, 1180, 1160, 1108, 1021, 773, 694 cm^{-1}; PMR(CD_2Cl_2): δ 6.9 - 8.2(m, Ph), 3.52 (m, CH), 1.33, 1.67 ppm(d, CH_3); ^{13}C NMR(CD_2Cl_2): δ 136.9(C_{ring}-N), 133.4(C_{ring}-Pd), 130.3($\underline{C}_{ring}$-Ph), 130.7, 129.2, 127.1, 123,1(Ph), 54.1, 52.9(CH), 21.9, 21.7 ppm(CH_3).

Anal. calcd for $C_{30}H_{38}Cl_4N_2Pd_2$: C, 46.12; H, 4.90; Cl, 18.15; N, 3.59.

Found : C, 45.94; H, 4.83; Cl, 18.47; N, 3.51.

Cis-$PdX_2(C_3RR')(PR''_3)$ (2a - f, 5). A solution of 1 (0.5 mmol) in methylene chloride (20 ml) was cooled to -78°C. To this solution was added phosphine (1 mmol) under vigorous stirring. The reaction mixture was allowed to warm up to room temperature and stirred for another 2 h. The solvent was removed and the residue was chromatographed on silica gel with methylene chloride / ether (3/1) as eluent to afford colorless crystals of 2a - f and 5.

Cis-$PdCl_2[C_3(Me_2N)_2](n\text{-}Bu_3P)$(2a) Recrystallization from chloroform /ether afforded colorless crystals of 2a in 85 % yield; mp. 172°C; IR(KBr): 2960, 2935, 2875, 1903, 1537, 1419, 1409, 1378, 1211 cm^{-1}; PMR($CDCl_3$): δ 3.24(br, NCH_3), 0.75 - 1.05 ppm(m, n-Bu); ^{13}C NMR($CDCl_3$): δ 150.6(C_{ring}-N), 125.0(C_{ring}-Pd), 41.2(br, NCH_3), 26.4 - 13.6 ppm(n-Bu); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 309 nm(2550).

Anal. calcd for $C_{19}H_{39}Cl_2N_2PPd$: C, 45.30; H, 7.80; Cl, 14.07; N, 5.56.

Found : C, 45.05; H, 7.68; Cl, 14.34; N, 5.62.

Cis-$PdCl_2[C_3(Et_2N)_2](n\text{-}Bu_3P)$(2b) - Recrystallization from methylene chloride/ether gave white crystals of 2b in 82 % yield: mp.142°C; IR(KBr): 2970, 1886, 1526, 1462, 1439, 1386, 1302, 1185, 1080 cm^{-1}; PMR($CDCl_3$): δ 3.57(m, CH_2), 1.31(t, CH_3), 0.75 - 1.05 ppm(m, n-Bu).

Anal. calcd for $C_{23}H_{47}Cl_2N_2PPd$: C, 49.39; H, 8.70; Cl, 12.76; N, 5.18.

Found : C, 49.34; H, 8.46; Cl, 12.60; N, 5.00.

Cis-$PdCl_2[C_3(i\text{-}Pr_2N)](n\text{-}Bu_3P)$(2c) - Recrystallization from methylene chloride/ether gave colorless crystals of 2c in 78 % yield: mp. 208°C

; IR(KBr): 2965, 1860, 1490, 1370, 1332, 1217, 1200, 1186, 1152, 1092, 1032 cm^{-1}; PMR($CDCl_3$): δ 4.09(m, CH), 0.75 - 1.05 ppm(m, n-Bu); ^{13}C NMR($CDCl_3$): δ 147.4(C_{ring}-N), 128.4(C_{ring}-Pd), 50.6(CH), 26.6 - 13.6 ppm(n-Bu, CH_3); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 310 nm(2760).

Anal. calcd for $C_{27}H_{55}Cl_2N_2PPd$: C, 58.40; H, 6.52; Cl, 10.66; N, 4.19.
Found : C. 58.63; H, 6.41; Cl, 10.49; N, 4.14.

Cis-$PdCl_2[C_3(i\text{-}Pr_2N)_2](Ph_3P)$(2d) - Recrystallization from methylene chloride/ ether afforded yellow crystals in 87 % yield: mp. 260°C(dec.); IR(KBr): 3050, 2970, 1853, 1495, 1435, 1371, 1337, 1156, 1095, 746, 696, 513 cm^{-1}; PMR($CDCl_3$): δ 7.20 - 7.90(m, Ph), 3.80(br, CH), 1.16, 1.24 ppm (d, CH_3).

Anal. calcd for $C_{33}H_{43}Cl_2N_2PPd$: C, 52.94; H, 8.17; Cl, 11.66; N, 4.53.
Found : C, 52.64; H, 9.00; Cl, 11.51; N, 4.55.

Cis-$PdCl_2[\overline{C_3N(t\text{-}Bu)CH_2CH_2CH_2(t\text{-}Bu)N}](n\text{-}Bu_2P)$(2e) - Recrystallization from methylene chloride/ether gave colorless crystals of 2e in 86 % yield: mp. 218°C: IR(KBr): 2965, 1880, 1466, 1341, 1325, 1277, 1214, 1068, 749 cm^{-1}; PMR($CDCl_3$): δ 3.43(t, NCH_2), 1.60(s, CH_3), 1.40(m, CH_2), 0.75 - 1.05 ppm(m, n-Bu); ^{13}C NMR(CD_2Cl_2): δ 150.5(C_{ring}-N), 122.7 (C_{ring}-Pd), 58.6($\underline{C}CH_3$), 50.4(NCH_2), 28.9(CH_3), 30.9 - 13.7 ppm(n-Bu, CH_2).

Anal. calcd for $C_{26}H_{51}Cl_2N_2PPd$: C, 51.82; H, 8.74; Cl, 11.71; N, 4.71.
Found : C, 52.05; H, 8.57; Cl, 11.82; N, 4.67.

Cis-$PdCl_2[C_3(i\text{-}Pr_2N)Ph](Ph_3P)$(5) - Recrystallization from methylene chloride/ether gave pale yellow crystals in 58 % yield: mp. 207°C (dec.); IR(KBr): 3050, 2970, 1840, 1515, 1479, 1440, 1340, 1164, 1102,

754, 699 cm^{-1}; PMR($CDCl_3$): δ 7.20 - 7.98(m, Ph), 3.90(br, CH), 1.43, 1.23 ppm(d, CH_3).

Anal. calcd for $C_{33}H_{34}Cl_2NPPd$: C, 60.55; H, 5.12; Cl, 11.20; N, 2.22.
Found : C, 60.75; H, 5.25; Cl, 10.86; N, 2.15.

$PdCl_2[C_3(Me_2N)_2](py)$ (2f). This was obtained by stirring 1a (0.5 mmol) in pyridine (10 ml) for 2 h and adding 10 ml of ether to this solution, which afforded yellow crystals in 88 % yield: mp. 151°C (dec.); IR(KBr): 3050, 2930, 1920, 1887, 1601, 1561, 1449, 1408, 1387, 1213, 1069, 1017, 765, 700 cm^{-1}; PMR($CDCl_3$): δ 8.90 - 9.10, 7.30 - 7.45 (py), 3.30 ppm(br, CH_3);

Anal. calcd for $C_{12}H_{17}Cl_2N_3Pd$: C, 37.87; H, 4.50; Cl, 18.63; N, 11.04.
Found : C, 37.63; H, 4.63; Cl, 18.35; N, 11.00.

Trans-$PdCl(C_3RR')(R''_3P)_2\cdot ClO_4$ (3a - c, e). A solution of 2(0.1 ml) in methylene chloride(10 ml) was cooled to -78°C. To this solution was added phosphine(0.1 mmol) under stirring. After stirring for another 2 h at room temperature, the reaction mixture was washed with 0.1 % $HClO_4$ aq. and extracted with methylene chloride. The solvent was removed and the residue was chromatographed on silica gel with methylene chloride/ether(3/1) to afford crystals of 3a - c, e.

Trans- $PdCl[C_3(Me_2N)_2](n\text{-}Bu_3P)_2\cdot ClO_4$(3a) - Recrystallization from hexane/acetone afforded colorless crystals in 71 % yield: mp. 129°C ; IR(KBr): 2965, 1903, 1567, 1460, 1406, 1376, 1210, 1143, 1090, 624 cm^{-1}; PMR($CDCl_3$): δ 3.27(s, CH_3), 0.75 - 1.90 ppm(m, n-Bu); ^{13}C NMR ($CDCl_3$): δ 151.6(C_{ring}-N), 122.0(C_{ring}-Pd), 39.5, 42.5(br, CH_3), 13.7 - 26.5 ppm(n-Bu); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 279(3457).

Anal. calcd for $C_{31}H_{66}Cl_2N_2O_4P_2Pd$: C, 48,35; H, 8.64; Cl, 9.21; N, 3.64.

Found : C, 48.30; H, 8.51; Cl, 9.45; N, 3.92.

Trans-$PdCl[C_3(Me_2N)_2](Ph_3P)_2 \cdot ClO_4$(3b) - Recrystallization from methylene chloride/ether afforded pale yellow crystals of 3b in 95 % yield: mp. 240°C(dec.); IR(KBr): 3050, 2940, 1901, 1563, 1438, 1435, 1408, 1386, 1210, 1090, 748, 699 cm^{-1}; PMR($CDCl_3$): δ 7.30 - 7.80(m, Ph), 2.57, 2.74 ppm(s, CH_3).

Anal. calcd for $C_{43}H_{42}Cl_2N_2O_4P_2Pd$: C, 58.03; H, 4.76; Cl, 7.97; N, 3.15.

Found : C, 57.85; H, 4.85; Cl, 8.11; N, 3.09.

Trans-$PdCl[C_3(Et_2N)_2](n\text{-}Bu_3P)_2 \cdot ClO_4$(3c) - Recrystallization from hexane/acetone gave colorless crystals of 3c in 89 % yield: mp. 78 °C; IR(KBr): 2960, 1886, 1523, 1464, 1443, 1385, 1294, 1214, 1184, 1090, 733, 621 cm^{-1}; PMR($CDCl_3$): δ 3.60(m, CH_2), 1.36(t, CH_3), 0.75 - 1.90 ppm(m, n-Bu); ^{13}C NMR($CDCl_3$): δ 150.1(C_{ring}-N), 123.0(C_{ring}-Pd), 46.5, 45.4(CH_2), 13.7 - 26.6 ppm(n-Bu, CH_3).

Anal. calcd for $C_{35}H_{74}Cl_2N_2O_4P_2Pd$: C, 55.88; H, 5.48; Cl, 12.66; N, 4.46.

Found : C, 56.19; H, 5.69; Cl, 12.44; N, 4.52.

Trans-$PdCl[\overline{C_3\text{-}N(t\text{-}Bu)CH_2CH_2CH_2(t\text{-}Bu)N}](n\text{-}Bu_3P)_2 \cdot ClO_4$(3e) Recrystallization from methylene chloride/ether gave colorless crystals in 94 % yield: mp. 137°C; IR(KBr): 2970, 1880, 1537, 1471, 1348, 1316, 1281, 1218, 1090, 627 cm^{-1}; PMR($CDCl_3$): δ 3.65(m, NCH_2), 1.52(s, CH_3), 0.90 - 1.90 ppm(m, n-Bu, CH_2); ^{13}C NMR($CDCl_3$): δ 150.5 (C_{ring}-N), 117.7(C_{ring}-Pd), 59.1(CCH_3), 50.8(NCH_2), 13.7 - 29.0 ppm (n-Bu, CH_2).

Anal. calcd for $C_{38}H_{78}Cl_2N_2O_4P_2Pd$: C, 52.68; H, 9.08; Cl, 8.18; N, 3.23.

Found : C, 52.71; H, 9.15; Cl, 8.33; N, 3.25.

Trans-ML'[C_3(i-$Pr_2N)_2$](n-$Bu_3P)_2\cdot ClO_4$(3d, f g). Bis(di-i-propylamino)cyclopropenium perchlorate(0.3 mmol) was suspended in 20 ml of dry deoxygenated ether and warmed to 30°C under argon atmosphere. To this was added 0.5 ml of 15 % n-BuLi/hexane with stirring. The suspension turned homogeneous. After cooling this solution to 0°C, trans-(n-$Bu_3P)_2$ML'Cl in ether was added with stirring. The reaction mixture was poured into 0.1 % $HClO_4$ aq. and extracted with methylene chloride. The solvent was removed and the residue was chromatographed on silica gel with methylene chloride / ether (3/1).

Trans-PdCl[C_3(i-$Pr_2N)_2$](n-$Bu_3P)_2\cdot ClO_4$(3d) - Crystallization from ethanol/ether gave colorless crystals in 67 % yield: mp. 120°C; IR(KBr): 2955, 1854, 1494, 1456, 1380, 1361, 1350, 1324, 1150, 1090, 1031, 621 cm^{-1}; PMR($CDCl_3$): δ 4.20(m, CH), 1.40(d, CH_3), 0.70 - 2.03 ppm(m, n-Bu); ^{13}C NMR($CDCl_3$): δ 147.8(C_{ring}-N), 125.6(C_{ring}-Pd), 50.8 (CH), 13.6 - 26.6 ppm(n-Bu, CH_3).

Anal. calcd for $C_{39}H_{82}Cl_2N_2O_4P_2Pd$: C, 53.09; H, 9.37; Cl, 8.04; N, 3.17.

Found : C, 52.85; H, 9.58; Cl, 8.19; N, 3.19.

Trans-PtCl[C_3(i-$Pr_2N)_2$](n-$Bu_3P)_2\cdot ClO_4$(3f) - Crystallization from ethanol/ether afforded pale yellow crystals in 43 % yield: mp. 154 °C; IR(KBr): 2960, 1860, 1497, 1462, 1380, 1360, 1198, 1150, 1090, 1032, 621 cm^{-1}; PMR($CDCl_3$): δ 4.03(m, CH), 1.34(d, CH_3), 0.75 - 2.30 ppm(m, n-Bu); ^{13}C NMR($CDCl_3$): δ 144.6(C_{ring}-N), 50.6(CH), 13.7 - 26.9 ppm(n-Bu, CH_3).

Anal. calcd for $C_{39}H_{82}Cl_2N_2O_4P_2Pt$: C, 48.24; H, 8.51; Cl, 7.30; N, 2.88.

Found : C, 48.57; H, 8.19; Cl, 7.70; N, 2.98.

Trans-Rh(CO)[C_3(i-$Pr_2N)_2$](n-$Bu_3P)_2 \cdot ClO_4$(3g) Crystallization from methylene chloride/ether gave yellow crystals in 43 % yield: mp. 195°C; IR(KBr): 2960, 1972, 1858, 1485, 1467, 1378, 1361, 1324, 1155, 1090, 1031, 621 cm^{-1}; PMR($CDCl_3$); δ 4.10(m, CH), 1.37(d, CH_3), 0.70 - 1.89 ppm(m, n-Bu); ^{13}C NMR($CDCl_3$); δ 149.9(C_{ring}-N), 147.8(C_{ring}-Rh), 192.2(CO), 50.1(CH), 26.9(CH_3), 13.6 - 27.8 ppm(n-Bu).

Anal. calcd for $C_{40}H_{82}ClN_2O_5P_2Rh$: C, 55.13; H, 9.49; Cl, 13.38; N, 3.22.

Found : C, 55.01; H, 9.78; Cl, 13.48; N, 3.32.

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CHAPTER 3

X-RAY CRYSTALLOGRAPHIC STUDY FOR BISAMINOCYCLOPROPENYLIDENE PALLADIUM

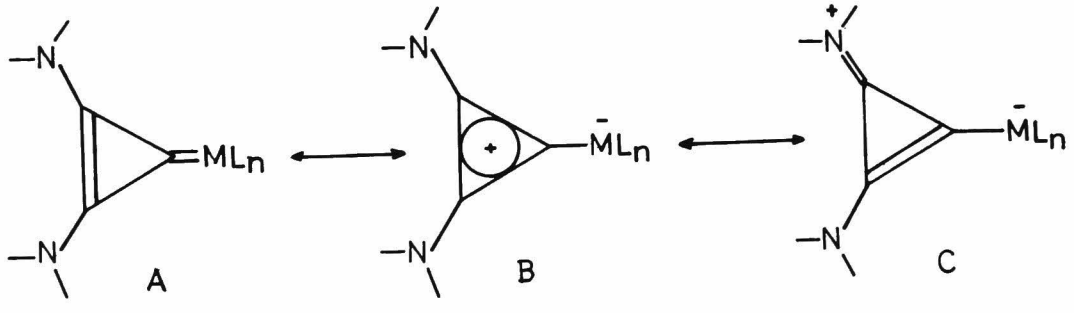
SUMMARY

The first precise analysis of the structure of a cyclopropenylidene transition metal complex has been carried out. The C-3 ring is bound with one of the three carbon atoms to the metal center with a Pd - C distance of 1.961(3) Å and is roughly perpendicular to the square plane of the metal. All C - C ring distances are equivalent within experimental error, 1.383(2) Å in average. Nitrogen atoms of the dimethylamino groups are sp^2 hybridized and these groups are co-planar with the C-3 ring. The results from MINDO/3 MO calculation for such a system are also discussed in comparison with the above results.

INTRODUCTION

Syntheses of a series of cyclopropenylidene complexes in which the ring system is stabilized by introducing dialkylamino groups at carbon atoms away from the metal have been successfully performed (Chapter 2). Based on infrared as well as ^{13}C-NMR spectral data the neutral complexes $PdCl_2[C_3(NR_2)_2](R'_3P)$ were proposed to have cis configuration and considerably weakened conjugation between the amino substituents and the C-3 ring was inferred. In this chapter are described the results of X-ray crystallographic study of a representative member of the series, cis-$PdCl_2[C_3(NMe_2)_2](n\text{-}Bu_3P)$ 1, undertaken to provide unequivocal evidence for the predicted structures based on spectroscopic data.

Following canonical forms may be written to represent formal bondings in these complexes.



To my knowledge, the only example reporting structures of cyclopropenylidene metal complexes is that of $Cr(CO)_5(C_3Ph_2)$.[1] The structural study, dating to 1969,[2] is not of sufficient accuracy to allow any assessments about the relative importance of the canonical forms A - C.

In this chapter is also discussed orbital interaction between cyclopropenylidene ligand and metal center on the basis of the results from MINDO/3 MO calculation with bisaminocyclopropenylidene.

RESULTS AND DISCUSSION

As illustrated by the packing diagram of Fig. 1, the crystal structure of cis-$PdCl_2[C_3(NMe_2)_2](n\text{-}Bu_3P)$ 1 consists of discrete molecuar units with no unusual intermolecular constants. Intermolecular distances and angles are given in Table 1.

The molecular structure of the complex, along with the numbering used, is shown in Fig. 2. Fig. 3 displays the carbocyclic backbone and co-ordination sphere of the metal, together with some important distances and angles. Geometry of the complex in whole is, as anticipated, square-planar arround the metal. Two chloro ligands are cis to each other, and cyclopropenylidene ring is bonded to the metal with one of the ring carbon atoms C(1). Also, as was observed in similar platinum-

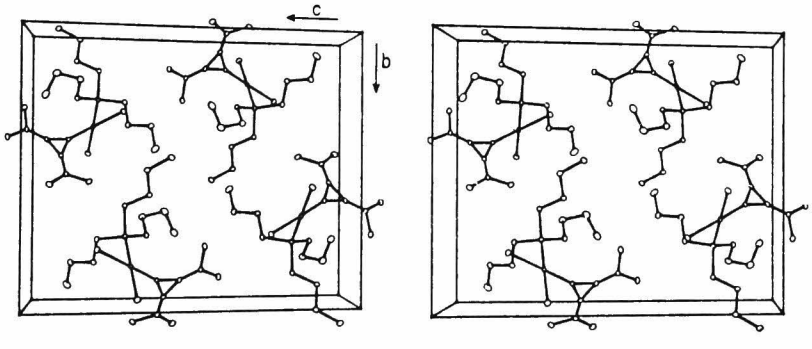


Fig. 1. A stereo view of the unit cell of *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$. Twenty percent probability ellipsoids are plotted.

TABLE 1

SELECTED DISTANCES (Å) AND ANGLES (deg) IN *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$

Bond distance (Å)			
Pd—Cl(1)	2.385(1)	P—C(11)	1.821(4)
Pd—Cl(2)	2.361(1)	P—C(21)	1.824(4)
Pd—P	2.238(1)	P—C(31)	1.798(4)
Pd—C(1)	1.961(3)	C(11)—C(12)	1.523(5)
C(1)—C(2)	1.385(5)	C(21)—C(22)	1.531(5)
C(1)—C(3)	1.380(4)	C(31)—C(32)	1.525(5)
C(2)—C(3)	1.384(5)	C(12)—C(13)	1.518(5)
C(2)—N(1)	1.316(4)	C(22)—C(23)	1.528(5)
C(3)—N(2)	1.324(4)	C(32)—C(33)	1.561(6)
N(1)—C(4)	1.455(5)	C(13)—C(14)	1.510(6)
N(1)—C(5)	1.455(5)	C(23)—C(24)	1.516(5)
N(2)—C(6)	1.459(5)	C(33)—C(34)	1.483(6)
N(2)—C(7)	1.456(4)		

Bond angle (deg)			
Cl(1)—Pd—Cl(2)	92.55(4)	C(2)—N(1)—C(5)	119.0(3)
Cl(1)—Pd—P	179.25(3)	C(3)—N(2)—C(6)	118.9(3)
Cl(1)—Pd—C(1)	89.7(1)	C(4)—N(1)—C(5)	116.9(3)
Cl(2)—Pd—P	87.25(4)	C(6)—N(2)—C(7)	117.3(3)
Cl(2)—Pd—C(1)	176.5(1)	Pd—P—C(11)	112.0(1)
P—Pd—C(1)	90.6(1)	Pd—P—C(21)	113.5(1)
Pd—C(1)—C(2)	147.7(3)	Pd—P—C(31)	116.1(1)
Pd—C(1)—C(3)	152.1(3)	C(11)—P—C(21)	103.6(2)
C(2)—C(1)—C(3)	60.1(2)	C(11)—P—C(31)	105.2(2)
C(1)—C(2)—C(3)	59.8(2)	C(21)—P—C(31)	105.3(2)
C(1)—C(3)—C(2)	60.1(2)	P—C(11)—C(12)	114.6(3)
C(1)—C(2)—N(1)	148.3(3)	P—C(21)—C(22)	115.1(2)
C(1)—C(3)—N(2)	148.3(3)	P—C(31)—C(32)	117.0(3)
N(1)—C(2)—C(3)	151.9(3)	C(11)—C(12)—C(13)	111.2(3)
N(2)—C(3)—C(2)	151.6(3)	C(21)—C(22)—C(23)	111.2(3)
C(2)—N(1)—C(4)	122.1(3)	C(31)—C(32)—C(33)	110.7(3)
C(3)—N(2)—C(7)	122.2(3)	C(12)—C(13)—C(14)	112.8(3)
C(22)—C(23)—C(24)	113.6(3)		
C(32)—C(33)—C(34)	112.9(3)		

Torsion angle (deg)	
C(1)—Pd—P—C(11)	−113.7(2)
C(1)—Pd—P—C(21)	129.4(2)
C(1)—Pd—P—C(31)	7.1(2)

Average deviation (Å) from least-squares plane; $Ax + By + Cz = D$

	Dev.	*A*	*B*	*C*	*D*
Plane 1 (Pd, Cl(1), Cl(2), P, C(1))	0.025	3.657	9.793	10.261	4.953
Plane 2 (C(1), C(2), C(3), N(1), N(2))	0.006	6.049	−8.972	2.727	−0.267
Plane 3 (C(1), C(2), C(3), N(1), N(2), (C(4), C(5), C(6), C(7))	0.076	5.922	−9.164	3.099	−0.154
Plane 4 (P, C(11), C(12), C(13), C(14))	0.008	6.648	−6.164	−10.333	−5.788
Plane 5 (P, C(21), C(22), C(23), C(24))	0.047	7.324	−5.887	−4.671	−4.163

Interplanar angle (deg)	
Plane 1—Plane 2	80.3

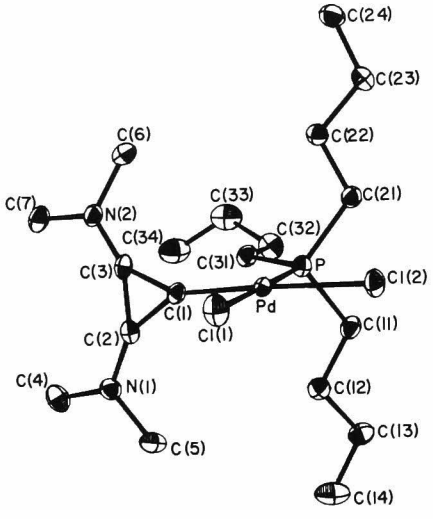


Fig. 2. Molecular structure of *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$. The thermal ellipsoids correspond to 50% probability enclosures. Hydrogen atoms have been omitted.

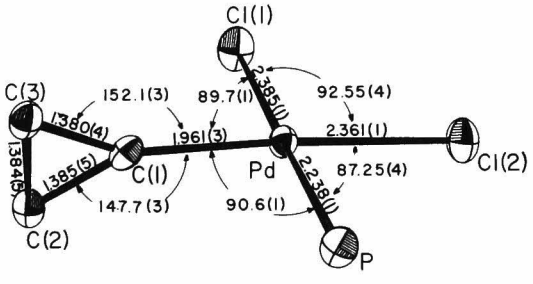


Fig. 3. A perspective view of the inner coordination sphere of *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$ with important distances and angles. The thermal ellipsoids are drawn at the 50% probability level.

group metal complexes containing acyclic carbene ligands,[3] the plane of the three-membered ring is nearly perpendicular to the square-plane of the metal, and the dihedral angle between the best plane involving C(1), C(2), C(3), N(1), N(2) and that involving Pd, Cl(1), Cl(2), P, C(1) is 80.3° (Table 1).

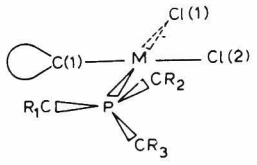
In this structure there is a high degree of equivalence in the metric parameters with the chemically equivalent bonds of the cyclopropenylidene ligands.

Co-ordination arround the Palladium Atom. Geometry of the metal is **square**-planar with the average deviation of the plane-defining atoms [Pd, Cl(1), Cl(2), P, and C(1)] from their best plane being only 0.025 Å. In addition this plane is roughly a molecular mirror plane. However, in contrast to the case of related molecule cis-$PtCl_2[-\overline{CNPh(CH_2)_2NPh}]-(Et_3P)$[3] in which corresponding plane exactly coincides with a crystallographic mirror plane, in 1 the symmetry is broken by the "slipped" carbene ligand (vide infra) and one butyl group[C(31) through C(34)] of the phosphine ligand. Within the PdL_4 plane deviations from right angles are generally small, the chloro ligands forming the largest cis angle [92.55(4)°] presumably because of mutual electron cloud repulsions in dominance over many other factors involved.

The Pd - Cl bond lengths are 2.385(1) and 2.361(1) Å for Cl(1) and Cl(2), respectively. The difference amounts to as much as 0.024(2) Å, while these two values are well within the range of 2.24 to 2.45 Å observed for other Pd^{II} - Cl bonds.[4] In view of the experimentally identical distances of the two Pt - Cl bonds of cis-$PtCl_2[-\overline{CNPh(CH_2)_2NPh}](Et_3P)$

TABLE 2

COMPARATIVE BOND DISTANCES AND ANGLES IN RELATED METAL—CARBOCYCLIC CARBENE COMPLEXES



	cis-$PdCl_2[C(Me_2NC)_2]$-$(P\text{-}n\text{-}Bu_3)$[a]	*cis*-$PtCl_2(\text{-}\overline{C\text{-}NPh\text{-}(CH_2)_2\text{-}NPh}\text{-})(PEt_3)$[b]
M—P	2.238(1) Å	2.234(3) Å
M—Cl(1)	2.385(1) Å	2.381(3) Å
M—Cl(2)	2.361(1) Å	2.362(3) Å
P—CR(2,3)[c]	1.824(4) and 1.821(4) Å	1.823(13) Å
P—CR(1)	1.798(4) Å	1.796(16) Å
M—P—CR(2,3)	112.0(1) and 113.5(1)°	112.0(4)°
M—P—CR(1)	116.1(1)°	116.3(5)°
C(1)—M—P—CR(1)	7.1(2)°	0°[d]

[a] This work. [b] Ref. 3. [c] Refer to sketch in upper left of table for notation. [d] Constrained by crystallographic mirror symmetry.

(Table 2), the trans influence which was ascribed to this complex[3] should also be applied to the present case. The Pd P bond distance of 2.238(1) Å is not unusual. With palladium(II) complexes bearing chloro ligands trans to P, Pd P bond lengths have been observed between 2.219 (4)[5] and 2.260(2) Å.[6] Two of the three butyl groups of the $P(n\text{-}Bu)_3$ ligand are in planar zig-zag conformations where the steric repulsions between hydrogen atoms on adjacent carbon atoms are minimized.[7] The third alkyl chain, which is eclipsed with respect to the Pd - C(1) bond when viewed down to the Pd - P vector, takes a helical conformation. The P - C bond lengths and their angles also reflect the disparate nature of this third butyl group. These P C distances and M - P - C bond angles are close to the corresponding values reported for cis-$PtCl_2[\text{-}\overline{CNPh(CH_2)_2\text{-}NPh}](Et_3P)$,[3] although no mention was made about this disparity possibly owing to the rather higher standard deviations estimated for this platinum complex (Table 2).

The bond distance 1.963(3) Å for Pd - C(1) is somewhat shorter for ordinary Pd - C single bond length, even though hybridization is taken into account. For example Pd - C(sp^2) distances of the metal σ-vinyl bonds in cis-bis[1,2-bis(trifluoromethyl)-3-acetyl-4-oxo-pent-1-enyl-O,C] palladium (II) are 1.993 Å[8] in average.

The Bis(dimethylamino)cyclopropenylidene Ligand. An approximate molecular mirror plane is defined by the metal and four atoms bound to it, the largest deviation from this symmetry being found with the "slipped" carbocyclic ligand. Atom C(2) is 0.880 Å apart from the plane 1 (Table 1) while atom C(3) is only 0.479 Å away from the plane in the opposite side. No unusual nonbonding contacts which would account for this tilt are seen between the two distal methyl groups of the bis(dimethylamino)cyclopropenylidene ligand. Furthermore, if steric crowding were the case of this displacement, then a significant dissymmetry of the bond angles C(1) - C(2) - N(1) [148.3(3)°] and C(1) C(3) - N(2) [148.3(3)°] should be expected. This tilt is reminiscent of the π-bound ethylene group in Zeise's salt,[9] which is 5.9° away from the normal to square plane of the platinum. No such symmetry was reported for the 2,3-bisphenylcyclopropenylidene ligand in $Cr(CO)_5(C_3Ph_2)$.[1] The nitrogen atoms which are sp^2 hybridized and co-planar with the C-3 ring are bonded at a 1.320(4) Å distance from the ring carbon atoms. This distance is markedly shorter than C - N single bond distance of 1.475(5) Å observed for CH_3NH_2.[10] Judging from the high symmetry of the C-3 ring, with uniform bond distribution, the π-back donation from the Pd atom seems to be comparable in its magnitude to the electron releasing from the

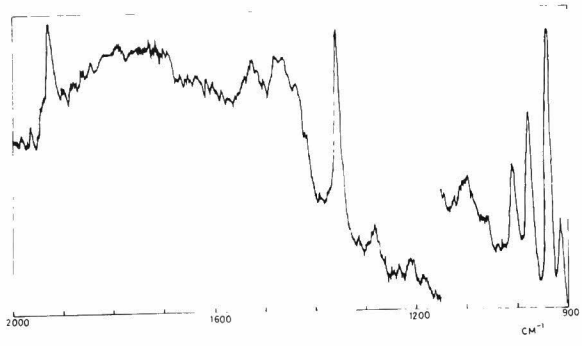


Fig. 4. Laser ramman spectrum of cis-$PdCl_2[C_3(Me_2N)_2](n\text{-}Bu_3P)$ 1.

dimethylamino groups. This is in good agreement with the results obtained from infrared and ^{13}C-NMR structural studies in the previous chapter. Participation of d_{xy} orbital of the metal in this back bonding would explain the angle of 80.3° between sequare plane of the metal and the least-square plane of the ligand. A reasoning that this dihedral angle could be a manifestation of steric factors may also be possible.

There are considerable differences in the average C_{ring}-C_{ring} and C_{ring}-N bond distances between the aromatic tris(dimethylamino)cyclopropenium cation [C_{ring}-C_{ring} 1.363(7), C_{ring}-N 1.333(7) Å][11] and the present case [C_{ring}-C_{ring} 1.383(2), C_{ring}-N 1.320(4) Å], though N-Me distances are the same in both cases. In infrared and laser ramman spectra, the above difference in average C_{ring}-C_{ring} distances are seen with the ring deformation vibrational bands at lower frequencies in the case of the present complex (1903 cm^{-1}), compared to the case of tris(dimethylamino)cyclopropenium cation (1985 cm^{-1}). As described in previous chapters, such bands at relatively lower frequencies are

generally observed with bisaminocyclopropenylidene palladium (II) complexes.

Preferred Canonical Forms. No simple description of the present structure appears possible in terms of canonical forms A - C. Form A (a carbene) is favored by short Pd C bond and suitable arrangement of the C-3 ring relative to the metal - ligands plane. However, shorter C - N bond lengths and planarity of the ring-nitrogen part of the complex favor form C. Equality of the three bond lengths within C-3 ring suggests comparable contribution of the two forms A and C. This also supports the conclusion in Chapter 2.

MINDO/3 MO Calculation. In the hope of elucidating further nature of interactions between bisaminocyclopropenylidene ligand and metal center, MINDO/3 MO calculations[12] have been carried out with a simplified model, bisaminocyclopropenylidene 2. In Table 3 are shown AO coefficients for the C-3 ring carbons in several molecular orbitals whose energy levels are close to nonbonding level. These molecular orbitals are shown schematically in Fig. 5, where the most significant

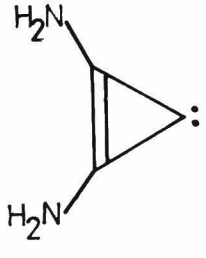


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Table 3 AO coefficients for C_3 ring carbons and energy levels on molecular orbitals in bisaminocyclopropenylidene.

Energy Level(ev)		-9.709	-8.023	-8.002	2.332	2.722	2.732
A.O. Coefficient							
C_1	2s	0.000	-0.392	0.000	0.000	0.000	0.079
	$2p_x$	0.000	-0.610	0.000	0.000	0.000	-0.235
	$2p_y$	0.615	0.000	0.000	0.322	0.000	-0.000
	$2p_z$	0.000	0.000	-0.457	0.000	0.817	0.000
C_2	2s	0.156	0.040	0.000	-0.339	0.000	-0.197
	$2p_x$	0.391	0.412	0.000	0.817	0.000	0.007
	$2p_y$	-0.023	0.208	0.000	-0.005	0.000	-0.251
	$2p_z$	0.000	0.000	-0.274	0.000	-0.382	0.000
C_3	2s	-0.156	0.040	0.000	0.339	0.000	-0.197
	$2p_x$	-0.391	0.412	0.000	-0.187	0.000	0.007
	$2p_y$	-0.023	-0.208	0.000	-0.005	0.000	0.251
	$2p_z$	0.000	0.000	-0.274	0.000	-0.382	0.000
		Ψ_{11}	Ψ_{12}	Ψ_{13}	Ψ_{14}	Ψ_{15}	Ψ_{16}

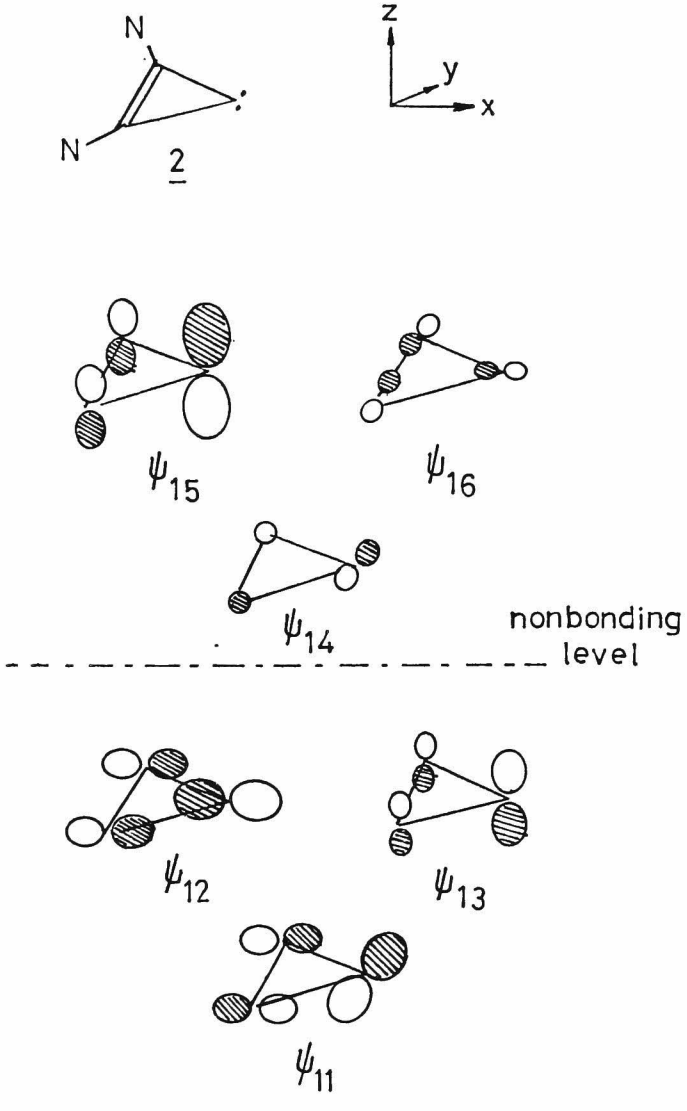
N
N
2
z
y
x
ψ_{15}
ψ_{16}
ψ_{14}
nonbonding
level
ψ_{12}
ψ_{13}
ψ_{11}

Fig. 5.

atomic orbitals for each carbon are illustrated. Orbitals Ψ_{11}, Ψ_{12} and Ψ_{13} are occupied orbitals while Ψ_{14}, Ψ_{15} and Ψ_{16} are unoccupied ones. In the case of d orbitals of the palladium (d^8), they split in the square planar ligand field so that $4d_{xy}$, $4d_{yz}$, $4d_{xz}$ and $4d_{y}2$ are all formally filled, while $4d_{x}2_{-z}2$ is vacant (square plane of the metal is placed in xz plane).

The bonding orbital Ψ_{11} mixes with $5p_y$ orbital of the palladium, while Ψ_{12} orbital donates electrons to its $4d_{x}2_{-z}2$, $5p_x$ and the orbitals 5s, and Ψ_{13} to its $5p_z$ orbital. On the other hand, vacant orbitals Ψ_{14} and Ψ_{15} have strict symmetries suitable for the overlappings with the filled palladium $4d_{xy}$ and $4d_{xz}$ orbitals, respectively. The vacant orbital Ψ_{16} also has symmetry available for an interaction with the filled $4d_{y}2$ orbital of palladium. The electron donation from bonding orbitals Ψ_{11}, Ψ_{12} and Ψ_{13} to vacant orbitals of the metal would weaken bonds among C-3 ring carbons. In addition, back donation from filled metal d orbital to antibonding orbital Ψ_{14} might also diminish each C - C bonding of the C-3 ring. The efficient interaction between orbital Ψ_{15} and the filled metal $4d_{xz}$ orbital is expected to result in enhanced metal - ligand π back donation. This reasoning seems suitable for interpretation of the spectroscopic and X-ray crystallographic observations described previously.

EXPERIMENTAL

Complex 1 was obtained as clear, colorless, well-formed crystals from acetone/hexane and stable in the air. Preliminary precession photographs revealed Laue symmetry 2/m. The extinction conditions observed, l=2n+1 for h0l, and k=2n+1 for 0k0, are consistent with the space group C_{2h}^5-$P2_1/c$. Least-squares refinement of the setting angles of nine reflections($20° < 2\theta(Mo\text{-}k_\alpha) < 27°$) with the sample at 22°C and of thirteen($19° < 2\theta(Mo\text{-}k_\alpha) < 31°$) at -160°C gave unit cell parameters of Table 4. Acquisition of a low temperature diffraction data set proceeded generally using methods by Ibers,[13] except that a low temperature device based closely on the design of Huffman[14] was employed.

Details of data collection are given in Table 4. Although the crystal maintained its chemical integrity throughout data collection, as judged by stability of the standard reflections, the originally transparent colorless crystal turned clear yellow-brown within the first 2 days in the X-ray beams.

The structure was successfully solved by conventional Patterson and Fourier methods using procedures and computer programs described in ref. 13). The positions of the atoms of the inner coordination sphere, Pd, Cl(1), Cl(2), P, C(1), were obtained from a three-dimensional origin-removed Patterson function. The positions of all nonhydrogen atoms were found on a subsequent difference Fourier map. In the penultimate difference Fourier map the positions of all methyl and methylene hydrogen atoms were apparent. This outcome was undoubtedly resulted from diminished thermal motions at -160°C. These

TABLE 4

CRYSTAL DATA, DATA COLLECTION PROCEDURES, AND REFINEMENT RESULTS FOR *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$

Formula	$C_{19}H_{39}Cl_2N_2P_1Pd_1$
Formula weight	503.82 amu
Space group	$C_{2h}^5\text{-}P2_1/c$
Cell constants at −160°C [22°C]	
a	7.933(4) Å [8.126(3) Å]
b	15.524(6) Å [15.527(7) Å]
c	19.572(7) Å [19.864(8) Å]
β	101.05(2)° [101.43(2)°]
V	2336 Å^3 [2457 Å^3]
Z	4
ρ_c (room temperature)	1.367 g/cm^3
ρ_0 (room temperature)	1.36 g/cm^3
ρ_c (−160°C)	1.414 g/cm^3
Data collection temperature	−160 ± 1°C
Crystal shape	a regular parallelepiped of approx. edge dimensions 0.20 mm × 0.18 mm × 0.16 mm, bounded by the faces {100}, {011}
Crystal volume	0.0052 mm^3
Radiation	Mo-K_α (λ(Mo-K_{α_1}) 0.70930 Å), monochromatized from (002) face of mosaic graphite
Linear absorption coefficient	10.7 cm^{-1}
Transmission factors	0.837—0.868
Detector aperture	3.0 mm by 3.0 mm
Take-off angle	2.5°
Scan speed	2.0° in 2θ/min
2θ limits	3.0—55.0°
Background counts	10 sec at each end of scan with rescan option
Scan range	0.8° below K_{α_1} to 0.8° above K_{α_2}
Data collected	$h \geq 0$, $k \geq 0$, $\pm l$
p	0.04
Unique data, $F_0^2 > 3\sigma(F_0^2)$	4383
Final number of variables	226
Error in observation of unit weight, electrons	1.12 e^-
R	0.036
R_w	0.042

positions were idealized(C-H 0.95 Å). The fixed contributions from these hydrogen atoms were included in the final cycle of least-squares refinement. All nonhydrogen atoms were refined anisotropically. The final refinement converged to values of R and R_W of 0.036 and 0.042, respectively, and to an error in an observation of unit weight of 1.12 electrons for the 226 variables and 4383 observations. The largest residual peak is of height 0.9(1) $e^-/Å^3$ on the final difference Fourier map. No unusual trends were indicated from an analysis of

TABLE 5

POSITION AND THERMAL PARAMETERS FOR *cis*-$PdCl_2[C((CH_3)_2NC)_2](P\text{-}n\text{-}Bu_3)$

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
PD	0.040566(31)	0.162941(16)	0.312631(12)	52.66(41)	13.13(11)	6.93(7)	-0.41(17)	5.50(11)	0.31(7)
CL(1)	0.26739(11)	0.059703(58)	0.331861(47)	93.8(15)	22.49(37)	16.87(24)	14.57(60)	14.33(48)	3.42(24)
CL(2)	0.13956(11)	0.225201(56)	0.217562(44)	95.4(15)	22.35(36)	11.94(22)	-0.28(59)	16.16(46)	2.89(22)
P	-0.16981(11)	0.261147(55)	0.295213(42)	68.0(14)	16.80(34)	10.10(21)	2.22(55)	5.12(42)	0.92(21)
C(1)	-0.05572(41)	0.11069(21)	0.36796(16)	59.7(52)	15.2(13)	7.77(80)	7.2(21)	1.5(16)	1.03(81)
C(2)	-0.15752(43)	0.04686(23)	0.40836(17)	58.9(55)	14.8(14)	10.85(88)	8.0(23)	10.2(18)	2.24(91)
C(3)	-0.08540(41)	0.10963(22)	0.45516(17)	50.3(50)	19.2(15)	9.02(84)	9.1(22)	5.4(17)	3.38(88)
N(1)	-0.25369(36)	-0.02186(18)	0.39157(15)	74.9(46)	17.4(12)	12.22(83)	-5.6(19)	9.2(16)	-0.35(80)
N(2)	-0.06124(38)	0.14623(19)	0.51738(14)	89.0(52)	17.8(14)	7.92(74)	3.0(21)	7.1(16)	0.52(78)
C(4)	-0.35570(49)	-0.05921(24)	0.43846(21)	79.7(67)	22.7(15)	20.6(12)	-4.0(26)	14.6(22)	3.8(11)
C(5)	-0.29621(52)	-0.04803(25)	0.31894(21)	98.6(74)	19.5(17)	16.3(11)	-7.7(29)	7.4(23)	-4.8(11)
C(6)	0.02093(52)	0.23063(26)	0.52675(20)	114.4(73)	26.9(18)	10.8(11)	-10.4(38)	1.1(23)	-2.3(11)
C(7)	-0.14832(49)	0.11622(26)	0.57201(19)	109.6(65)	28.3(18)	9.50(97)	3.8(28)	12.9(21)	1.8(11)
C(11)	-0.31095(45)	0.24829(25)	0.21074(18)	73.0(57)	23.7(17)	9.93(88)	0.9(26)	-0.3(18)	1.8(10)
C(12)	-0.40613(46)	0.16262(22)	0.20062(18)	78.3(61)	19.4(14)	13.29(92)	3.1(24)	6.9(19)	-0.68(93)
C(13)	-0.52417(46)	0.15825(24)	0.12983(20)	70.2(58)	26.1(16)	14.7(10)	1.6(25)	2.2(19)	-3.3(10)
C(14)	-0.61980(57)	0.07382(30)	0.11752(24)	131.1(81)	35.1(22)	27.4(14)	-15.5(35)	4.4(27)	-12.2(14)
C(21)	-0.09216(45)	0.37155(22)	0.29333(17)	81.7(62)	17.0(13)	10.41(90)	2.0(23)	6.4(19)	-0.21(88)
C(22)	-0.01511(46)	0.40984(23)	0.36459(19)	68.4(63)	15.8(14)	12.7(10)	1.8(24)	3.5(20)	0.18(95)
C(23)	0.07075(48)	0.49653(23)	0.35710(19)	80.6(67)	16.1(14)	15.9(11)	-1.8(25)	11.0(21)	1.19(96)
C(24)	0.13679(53)	0.54103(25)	0.42600(21)	120.4(73)	21.0(17)	17.0(12)	-12.3(29)	13.7(23)	-3.9(12)
C(31)	-0.30987(45)	0.26178(23)	0.35736(19)	79.7(59)	19.6(15)	10.8(18)	5.4(26)	2.4(19)	0.19(97)
C(32)	-0.45796(47)	0.32594(25)	0.34514(21)	77.0(60)	25.2(17)	20.8(11)	6.8(27)	6.1(21)	2.4(11)
C(33)	-0.52294(52)	0.34382(27)	0.41422(23)	101.8(69)	32.2(19)	28.0(14)	10.7(38)	5.1(25)	-5.8(13)
C(34)	-0.58565(57)	0.26514(30)	0.44433(24)	128.3(78)	42.4(22)	24.3(14)	-13.6(35)	21.9(27)	-10.0(14)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP(-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL))$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

$\Sigma\, w(|F_0| - |F_c|)^2$ as a function of $|F_0|$, setting angles, and Miller indices.

Final positional and thermal parameters are tabulated in Table 5. Root-mean-square amplitudes of vibration are given in Table 6. A table representing the values of $10\,|F_0|$ and $10\,|F_c|$ for the reflections used in the refinement is available.

The energy levels and AO coefficients of wave functions were computed for bisaminocyclopropenylidene using the established MINDO/3 MO method[12]. Geometrical parameters for the calculation are described in the experimental section of Chapter 1.

TABLE 6

ROOT-MEAN-SQUARE AMPLITUDE OF VIBRATION (Å) FOR *cis*-$PdCl_2[C(Me_2NC)_2](P\text{-}n\text{-}Bu_3)$

Atom	Minimum	Intermediate	Maximum
Pd	0.1097(6)	0.1268(5)	0.1204(5)
Cl(1)	0.138(2)	0.161(1)	0.202(1)
Cl(2)	0.121(2)	0.167(1)	0.183(1)
P	0.134(2)	0.141(1)	0.149(2)
C(1)	0.111(7)	0.130(6)	0.152(6)
C(2)	0.113(7)	0.126(7)	0.162(6)
C(3)	0.111(7)	0.123(6)	0.167(5)
N(1)	0.133(6)	0.147(5)	0.163(5)
N(2)	0.119(6)	0.146(6)	0.167(5)
C(4)	0,137(7)	0.170(6)	0.203(6)
C(5)	0.136(7)	0.175(6)	0.189(6)
C(6)	0.135(7)	0.175(7)	0.203(6)
C(7)	0.123(7)	0.179(6)	0.192(6)
C(11)	0.127(7)	0.160(6)	0.173(6)
C(12)	0.146(6)	0.158(6)	0.161(6)
C(13)	0.144(6)	0.159(6)	0.190(5)
C(14)	0.155(7)	0.216(6)	0.257(6)
C(21)	0.138(6)	0.144(6)	0.159(6)
C(22)	0.137(6)	0.145(7)	0.158(6)
C(23)	0.137(6)	0.153(7)	0.176(6)
C(24)	0.145(7)	0.170(6)	0.207(6)
C(31)	0.138(6)	0.149(6)	0.168(6)
C(32)	0.147(7)	0.179(6)	0.201(5)
C(33)	0.165(6)	0.195(6)	0.243(6)
C(34)	0.175(7)	0.189(6)	0.259(6)

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CHAPTER 4

SYNTHESES AND PROPERTIES OF BISPHENYL- AND BISALKYLCYCLOPROPENYLIDENE Pd COMPLEXES

SUMMARY

Several neutral and cationic palladium complexes of bisphenyl- and bisalkylcyclopropenylidenes, trans-X_2-μ-$X_2Pd(C_3R_2)$ (1: R= Ph, i-Pr, t-Bu; X= Cl, Br), cis-$PdX_2(C_3R_2)L$ (2: R= Ph, i-Pr, t-Bu; X= Cl; L= R'_3P, etc.) and trans-$PdX(C_3R_2)L_2 \cdot ClO_4$ (3: R= Ph, i-Pr, t-Bu; X= Cl; L= R'_3P) were synthesized. Infrared and ^{13}C-NMR spectra have been discussed to elucidate structures of these compounds.

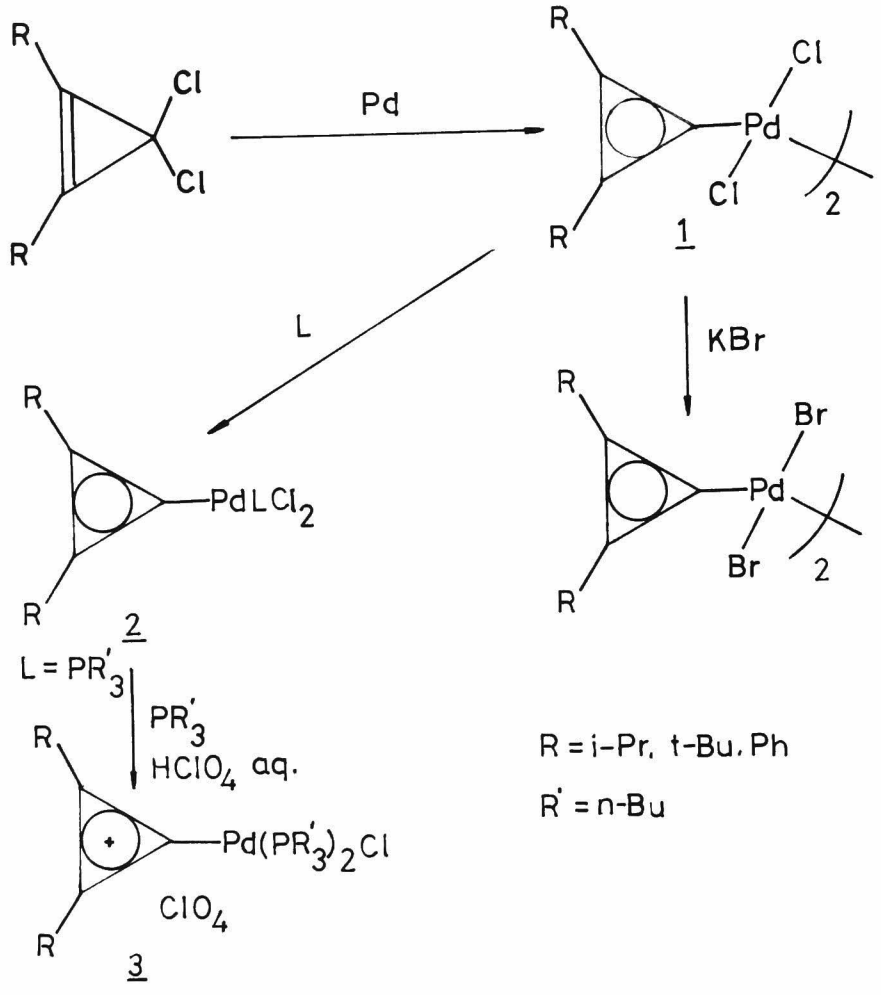
INTRODUCTION

Stable transition metal complexes of bisaminocyclopropenylidene have been successfully synthesized and their structures have become clear. However in these systems peripheral two amino groups would appreciably perturb the electronic situations at the ground state as well as at the excited states. Öfele reported the syntheses of some transition metal complexes of bisphenylcyclopropenylidene[1] but there has been no examples with bisalkylcyclopropenylidene.

In this chapter are described the syntheses and properties of palladium complexes of 2,3-bisalkylcyclopropenylidene, where π-conjugative interactions between the peripheral substituents and C-3 ring are considered to be small, with the use of their spectroscopic data. Such complexes should be more suitable for the investigation of the electronic nature of a cyclopropenylidene moiety.

RESULTS AND DISCUSSION

Synthesis. Di-μ-chloro complexes 1a and b were obtained according to a modified procedure for di-μ-chloro-dichloro-bis(phenyl)cyclopropenylidene-dipalladium, 1c.[1] A mixture of 3,3-dichloro-1,2-di-i-propylcyclopropene and slightly excess amounts of palladium black in freshly distilled benzene was kept at 90°C for 20h in an argon-replaced sealed tube. After the reaction mixture was filtered off, addition of ether to the filtrate gave orange crystals of 1a. As is seen in Fig. 1, it shows a characteristic ir band at 1787 cm^{-1} attributable to the deformation of C-3 ring. Furthermore, it exhibits tree bands at 347, 294 and 272 cm^{-1}



due to Pd - Cl stretching vibrations, indicating 1a to be a di-μ-chloro type complex.[2)]

To a cold solution (ca -60°C) of 1a in methylene chloride was added two molar amounts of tri-n-butylphosphine with stirring. After additional stirring for 2 h at room temperature, the product was recrystallized to afford mononuclear complex, 2a, as colorless crystals. Infrared spectrum of 2a reveals a characteristic band at 1787 cm^{-1} to be assigned to the ring deformation vibrational band of C-3 ring.

Table 1 Yields and properties of bisalkyl- and bisphenylcyclopropenylidene palladium 1a-3c.

	R	X	L	Yield(%)	M.P.(°C)	Color
1a	i-Pr	Cl		45	164	orange
1b	t-Bu	Cl		60	223(dec)	orange
1c	Ph	Cl		62	215(dec)	orange
1a	i-Pr	Br		95	172	reddish orange
2a	i-Pr	Cl	$n\text{-}Bu_3P$	69	153	white
2b	t-Bu	Cl	$n\text{-}Bu_3P$	75	153	white
2c	Ph	Cl	$n\text{-}Bu_3P$	63	205	white
2d	t-Bu	Cl	C_5H_5N	82	150	yellow
2e	t-Bu	Cl	CH_3CN	75	183(dec)	orange
2f	t-Bu	Cl	$(CH_3)_2SO$	67	202(dec)	yellow
3a	i-Pr	Cl	$n\text{-}Bu_3P$	92	151	white
3b	t-Bu	Cl	$n\text{-}Bu_3P$	68	164	white
3c	Ph	Cl	$n\text{-}Bu_3P$	94	135	white

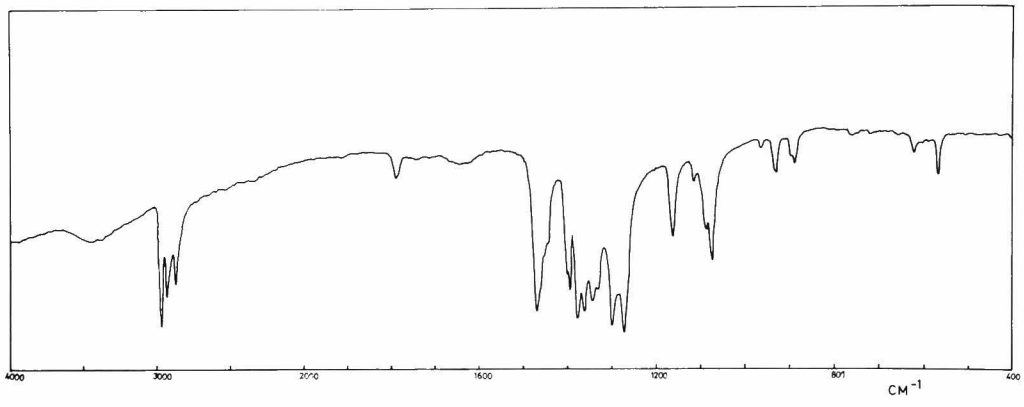


Fig. 1. Infrared spectrum of 1a.

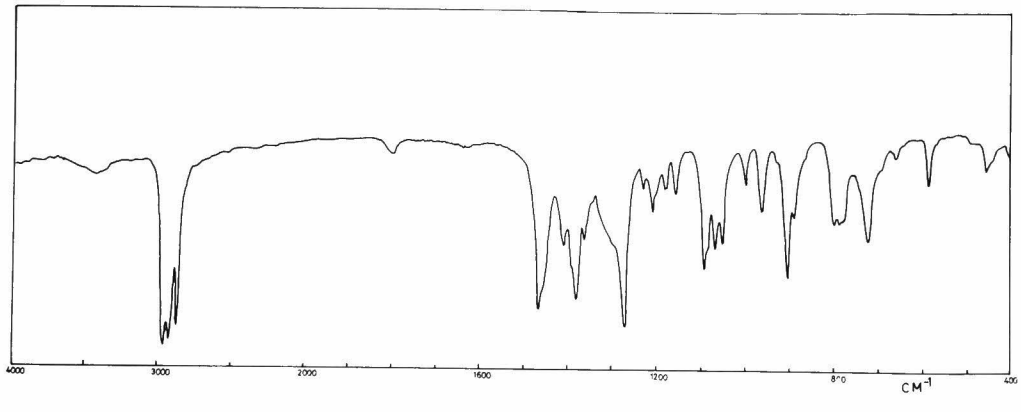


Fig. 2. Infrared spectrum of 2a.

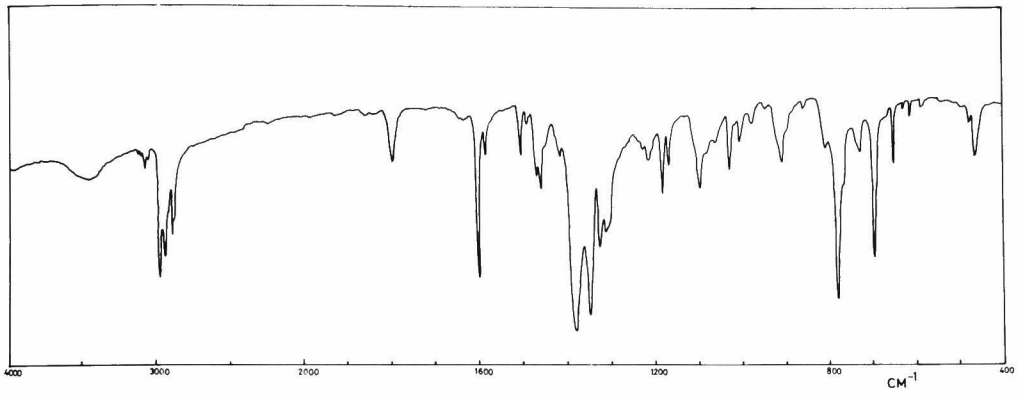


Fig. 3. Infrared spectrum of 2c.

A solution of 1a and 4 equiv. of tri-n-butylphosphine in methylene chloride was stirred at -60°C for 1 h. Treatment of the mixture with dil. aq. $HClO_4$ followed by recrystallization afforded a cationic complex 3a, which was also obtained by treatment of 2a with equimolar amount of tri-n-butylphosphine. By quite a similar manner, palladium complexes of bis-t-butylcyclopropenylidene and bisphenylcyclopropenylidene (1b 3c) are prepared.

Di-μ-chloro complex 1b and excess amounts of pyridine, acetonitrile and dimethyl sulfoxide gave the corresponding neutral complexes 2d - f (Table 1). Di-μ-chloro complex 1a by treatment with KBr in acetone gave corresponding di-μ-bromo complex 1a' as orange crystals. Above complexes are all stable in the air at room temperature. It is surprising that thermal stability of bisalkylcyclopropenylidene palladium is comparable to that of bisaminocyclopropenylidene palladium.

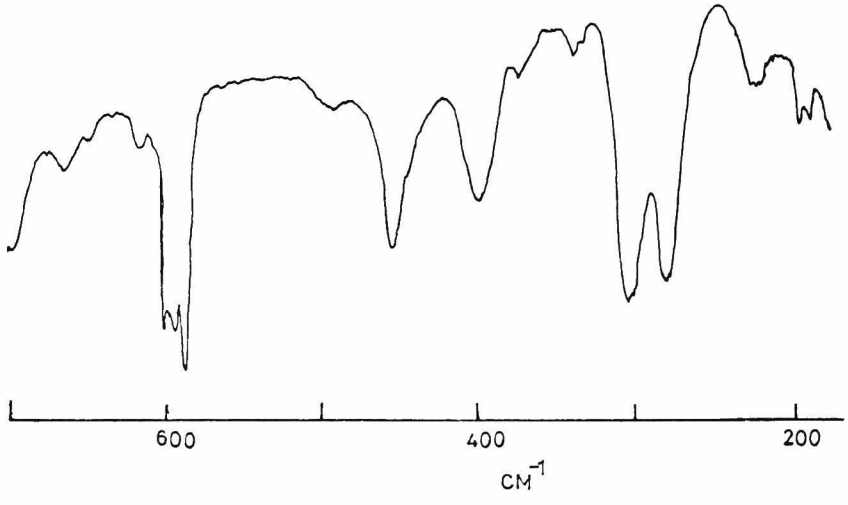


Fig. 4. Far-infrared spectrum of 2b (CeI).

Ligand Co-ordination. The configuration of neutral and cationic complexes of bisalkyl- and bisphenylcyclopropenylidene 2a - 3c should be the same with that of bisaminocyclopropenylidene. In infrared spectra the complexes 2a c exhibit two absorption bands corresponding to stretchings of two Pd - Cl bonds at 282 - 318 cm^{-1} (Table 2). In addition, small coupling constants $^{2}J(C_{carbene}$ - Pd - P) in Table 3 also suggest the cis configurations of 2a - c.[3,4] At the same time, each carbene carbon in 3a - c appears as a triplet with a small $^{2}J(C_{carbene}$ - Pd - P), indicating cationic complexes 3a - c should be the trans isomers.

The Cyclopropenylidene Ligands. In the ^{13}C-NMR spectra, C-3 ring carbons of bisalkylcyclopropenylidene palladium appear as two signals in the range of 180 - 206 ppm (Fig. 5). These are listed in Table 3 together with tose of bisaminocyclopropenylidene palladium 4a - c.

Table 2 Characteristic IR bands of cyclopropenylidene palladium.

	C_3 core (cm^{-1})	Pd - Cl
1a	1787	347, 294, 272
2a	1797	304, 292
2b	1780	305, 282
2c	1794	318, 282
3a	1788	---*
3b	1774	---*

*) Not observed in the range of 250 - 300 cm^{-1}.

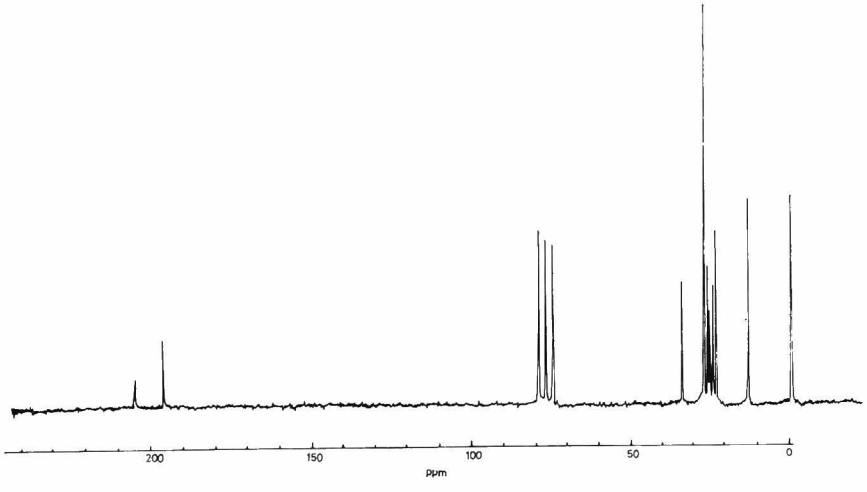


Fig. 5. ^{13}C NMR spectrum of 2b.

More deshielded one is assigned to the carbene carbon and the other to the two equivalent C-3 ring carbons. As far as the discussion is concerned a series of the complexes containing same cyclopropenylidene moieties, these chemical shifts for neutral complexes 2a - c and cationic complexes 3a c are similar to each other. The formal positive charge on 3a - c is

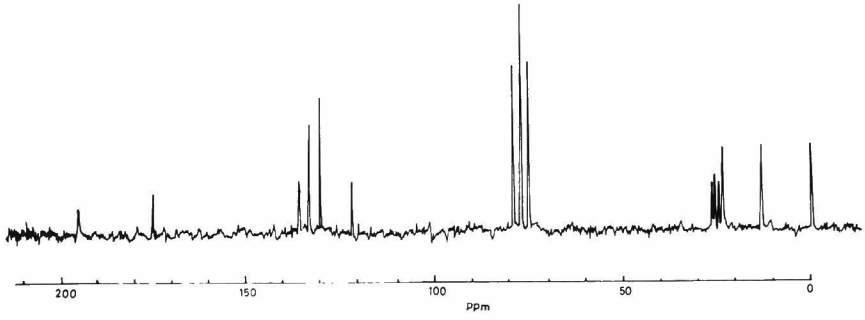
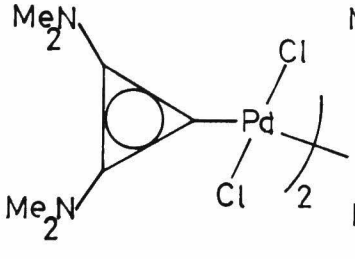


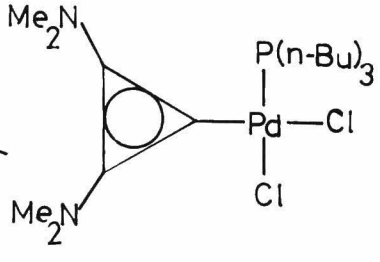
Fig. 6. ^{13}C NMR spectrum of 2c.

probably not existing in the cyclopropenylidene ligand.

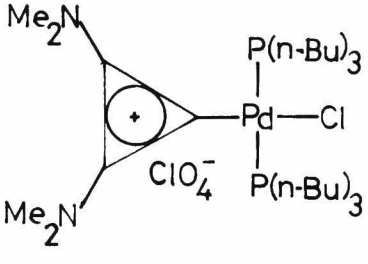
The ring carbons of neutral and cationic complexes are shielded in the decreasing order of bisaminocyclopropenylidene complexes ≫ bisphenylcyclopropenylidene complexes > bisalkylcyclopropenylidene complexes, suggesting that the electron densities on the C-3 ring carbons increase in the above order. Particular shielding of the ring carbons of bisaminocyclopropenylidene complexes are attributable to the considerable electron release from amino groups to C-3 ring. On the other hand taking account of the fact that the π-bonding effects paramagnetic



4a



4b



4c

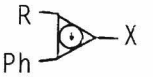
Table 3 ^{13}C Chemical shifts and coupling constants of C_3 ring on the complexes 1a - 4c.

Compd.	$\delta(C_{ring}\text{-}R)$	$\delta(C_{carbene})$		$^2J_{C_{ring}\text{-}P}$(Hz)	Solv.
1a	181.2	195.7			$CDCl_3$
1b	183.1	198.0			$CDCl_3$
2a	195.1	205.7	d	$\leqq$ 1.2	$CDCl_3$
2b	196.5	205.2	d	$\leqq$ 1.2	$CDCl_3$
2c	175.2	195.3	d	2.9	$CDCl_3$
3a	198.7	205.4	t	9.8	$CDCl_3$
3b	199.7	205.8	t	9.8	$CDCl_3$
3c	176.0	195.2	t	10.7	$CDCl_3$
4a	150.9	99.9			CD_2Cl_2
4b	150.6	120.5	d	6.1	$CDCl_3$
4c	151.6	122.0	t	10.5	$CDCl_3$

contribution to carbons and consequently causes the deshielding of them.[5] considerable deshielding of carbene carbon of bisalkylcyclopropenylidene complex seems to be due to considerable multi-bonding character of carbene carbon - metal center bonds. Furthermore $^2J(C_{carbene}\text{-}P)$ decreases in the order of 2a, b > 2c > 4b. The σ-bonding between carbene carbon and metal center might be diminished in this order.

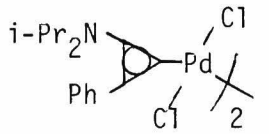
The chemical shifts of phenyl carbons in bisphenylcyclopropenylidene 2c and several bisphenylcyclopropenium cations are shown in Table 4. The p-carbon of the phenyl group is more shielded when it bears stronger electron donating substituents X. The chemical shift of p-carbon in 2c is close to those in bis(phenyl)-diethylaminocyclopropenium cation and in bis(phenyl)-ethoxycyclopropenium cation. Quite similar trend is also observed with o-carbons of the phenyl groups. This seems to be correlated

Table 4 ^{13}C-Chemical shifts of phenyl carbons on 2c, 5, and several cyclopropenium cations.



R	X	$\delta(C_{ipso})$	$\delta(C_{ortho})$	$\delta(C_{meta})$	$\delta(C_{para})$
Ph	H	128.5	133.7	131.3	140.3
Ph	Ph	120.2	136.0	131.3	139.3
Ph	OEt	131.2	135.7	135.2	137.3
Ph	NEt_2	129.3	132.3	130.3	135.1
2c		121.7	133.4	130.1	136.4
i-Pr_2N	H	120.2	133.4	130.6	136.5
i-Pr_2N	SMe	120.3	131.2	130.1	133.8
i-Pr_2N	OMe	120.1	131.3	129.8	133.0
i-Pr_2N	$N(i\text{-}Pr)_2$	126.5	129.5	128.8	130.4
5		123.4	129.8	129.2	130.7

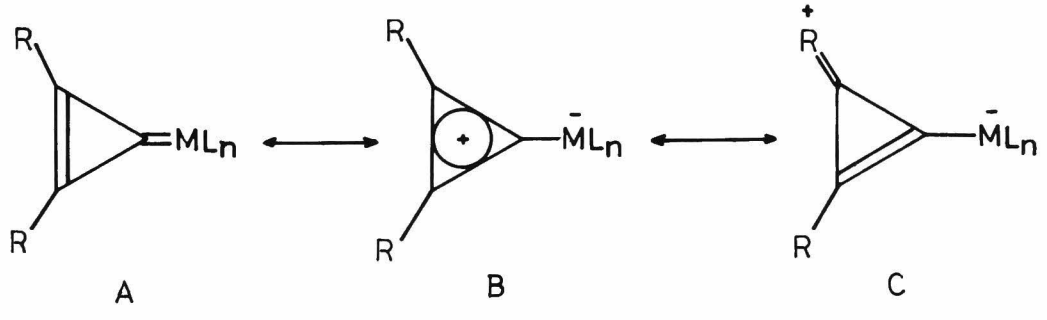
5)



with the effective π-back donation from Pd atom to the C-3 ring in bisphenylcyclopropenylidene palladium complexes. Analogous trend is observed with di-i-propylaminophenylcyclopropenylidene palladium complex 5 (Table 4).

The appreciable stability of bisalkyl- and bisphenylcyclopropenylidene palladium complexes should be largely due to the effective back donation from palladium d-orbital to cyclopropenylidene π*-orbital. Aromaticity of cyclopropenylidene system should also be one of significant reasons for this stability.

Following canonical forms A and B should be predominant with bisalkyl- and bisphenylcyclopropenylidene palladium complexes, while forms A and C are thought to be dominant with bisaminocyclopropenylidene palladium complexes.



EXPERIMENTAL

Trans-Cl_2-μ-Cl_2Pd(C_3R_2) (1a, b). A mixture of 1,2-bisalkyl-3,3-dichlorocyclopropene(1 mmol) and palladium black(1.1 mmol) in freshly distilled benzene was kept at 90°C in an argon-replaced sealed tube. After 20 h, the reaction mixture was filtered off. Addition of ether to the filtrate gave orange crystals of 1a and b in 45 % and 60 % yields, respectively.

Trans-Cl_2-μ-Cl_2Pd[C_3(i-Pr)$_2$] (1a) - mp. 164°C; IR(KBr): 2973, 1787, 1466, 1374, 1358, 1296, 1268, 1159, 1070 cm^{-1}; PMR($CDCl_3$): δ 3.41(sep, CH), 1.44 ppm(d, CH_3); ^{13}C NMR($CDCl_3$): δ 195.7(C_{ring}-Pd), 181.2(C_{ring}-C), 28.7(CH), 19.6 ppm(CH_3); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 364 nm (1088).

Anal. calcd for $C_{18}H_{28}Cl_4Pd_2$: C, 36.09; H, 4.71; Cl, 23.67.
Found : C, 36.29; H, 5.00; Cl, 23.47.

Trans-Cl_2-μ-Cl_2Pd[C_3(t-Bu)$_2$] (1b) mp. 223°C(dec.); IR(KBr): 2973, 1782, 1482, 1373, 1345, 1332, 1232, 1185 cm^{-1}; PMR($CDCl_3$): δ 1.48 ppm(s, CH_3); ^{13}C NMR($CDCl_3$): δ 198.0(C_{ring}-Pd), 183.1(C_{ring}-C), 34.7(C-CH_3), 27.7 ppm(CH_3); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 364 nm(4786).

Anal. calcd for $C_{22}H_{36}Cl_4Pd_2$: C, 40.33; H, 5.54; Cl, 21.65.
Found : C, 40.13; H, 5.52; Cl, 21.83.

Trans-Cl_2-μ-Cl_2Pd(C_3Ph_2) (1c). This was prepared according to the method reported by Öfele[1]: mp. 215°C; IR(KBr): 3055, 1790, 1598, 1388, 1343, 1339, 766, 684 cm^{-1}; PMR(CD_2Cl_2): δ 8.50 - 8.77, 7.80 - 8.07 ppm(m, Ph); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 250(66200), 297(59100), 361 nm(3200).

Trans-Br_2-μ-$Br_2Pd[C_3(i\text{-}Pr)_2]$ (1a'). This was prepared by stirring 1a(1 mmol) and large excess amounts of KBr in acetone(10 ml). Crystallization from methylene chloride/ether afforded reddish brown crystals of 1a' in 95 % yield; mp. 172°C; IR(KBr): 2973, 1780, 1483, 1373, 1342, 1331, 1233, 1181 cm^{-1}; PMR($CDCl_3$): δ 3.41(sep, CH), 1.44 ppm(d, CH_3); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 382 nm(2589).

Anal. calcd for $C_{18}H_{28}Br_4Pd_2$: C, 31.72; H, 4.36; Br, 38.37.
Found : C, 31.80; H, 4.61; Br, 38.40.

Cis-$PdX_2(C_3R_2)(PR'_3)$ (2a - c). A solution of 1a - c(0.5 mmol) in methylene chloride(20 ml) was cooled to -60°C. To this was added phosphine(1 mmol) under vigorous stirring. The reaction mixture was allowed to warm up to room temperature and stirred for additional 2 h. The solvent was removed and the residue was chromatographed on silica-gel with methylene chloride/ether(3/1) to afford colorless crystals of 2a c.

Cis-$Pd_2Cl_2[C_3(i\text{-}Pr)_2](n\text{-}Bu_3P)$ (2a) - Recrystallization from methylene chloride/ether afforded white crystals of 2a in 69 % yield: mp. 153°C; IR(KBr): 2965, 1797, 1470, 1382, 1273, 1092, 1078, 1051, 907, 801, 789, 724 cm^{-1}; PMR(CD_2Cl_2): δ 3.36(sep, CH), 1.50(d, CH_3), 0.80 - 1.80 ppm(m, n-Bu); ^{13}C NMR($CDCl_3$): δ 205.7(C_{ring}-Pd), 195.1 (C_{ring}-C), 28.8(CH), 19.6(CH_3), 13.6 26.4 ppm(n-Bu); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 306 nm(1794).

Anal. calcd for $C_{21}H_{41}Cl_2PPd$: C, 50.26; H, 8.24; Cl, 14.13.
Found : C, 50.11; H, 8.41; Cl, 14.19.

Cis-$PdCl_2[C_3(t\text{-}Bu)_2](n\text{-}Bu_3P)$ (2b) Recrystallization from methylene chloride/ether gave colorless crystals of 2b in 75 % yield; mp. 153°C; IR(KBr): 2965, 1780, 1481, 1474, 1374, 1342, 1238, 1175, 1090, 905, 801, 725, 693, 600 cm^{-1}; PMR(CD_2Cl_2): δ 1.52(s, CH_3), 0.80 - 1.80 ppm(m, n-Bu); ^{13}C NMR($CDCl_3$): δ 205.2(C_{ring}-Pd), 196.5($\underline{C}_{ring}$-C), 34.5 ($\underline{C}$-CH_3), 27.7(CH_3), 13.6 - 26.4 ppm(n-Bu); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 308 nm (2083).

Anal. calcd for $C_{23}H_{45}Cl_2PPd$: C, 52.14; H, 8.56; Cl, 13.38.

Found : C, 52.18; H, 8.73; Cl, 13.48.

Cis-$PdCl_2(C_3Ph_2)(n\text{-}Bu_3P)$ (2c) - Recrystallization from methylene chloride/ether afforded white crystals of 2c in 63 % yield; mp.205°C; IR(KBr): 3050, 2960, 1794, 1598, 1375, 1344, 1321, 1305, 773, 688 cm^{-1}; PMR(CD_2Cl_2): δ 8.35 - 8.60, 7.73 - 7.97(m, Ph), 0.75 - 1.05 ppm(m, n-Bu); ^{13}C NMR($CDCl_3$): δ 195.3(C_{ring}-Pd), 175.2($\underline{C}_{ring}$-Ph), 136.4, 133.4, 130.2, 121.9(Ph), 13.5 - 26.5 ppm(n-Bu).

Anal. calcd for $C_{27}H_{37}Cl_2PPd$: C, 56.97; H, 6.36; Cl, 12.70.

Found : C, 56.90; H, 6.54; Cl, 12.44.

$PdCl_2[C_3(t\text{-}Bu)_2](py)$ (2d). This was prepared by stirring 1b(0.5 mmol) in pyridine(10 ml) for 10 h. To this solution was added 10 ml of ether, which gave yellow crystals of 2d in 82 % yield: mp. 150°C; IR(KBr): 3075, 1604, 1479, 1445, 1375, 1347, 1217, 1103, 1070, 757, 695 cm^{-1}; PMR($CDCl_3$): δ 8.90 - 9.33, 7.20 - 7.70(m, py), 1.56 ppm(s, CH_3).

Anal. calcd for $C_{16}H_{23}Cl_2NPd$: C, 47.23; H, 5.70; Cl, 17.45; N, 3.45.

Found : C, 47.50; H, 5.84; Cl, 17.36; N, 3.62.

$PdCl_2[C_3(t\text{-}Bu)_2](CH_3CN)$ (2e). This was prepared by stirring 1b(0.5 mmol) in acetonitrile(10 ml) for 2 h. After evaporation to dryness under reduced pressure, crystallization from acetonitrile/ether afforded orange crystals of 2e in 75 % yield: mp. 183°C(dec); IR(KBr): 2973, 2280, 1782, 1482, 1373, 1345, 1332, 1232, 1185 cm^{-1}; PMR($CDCl_3$): δ 2.20 (s, CH_3), 1.48 ppm(s, t-Bu).

Anal. calcd for $C_{13}H_{21}Cl_2NPd$: C, 42.36; H, 5.74; Cl, 19.24; N, 3.80.
Found : C, 42.64; H, 5.85; Cl; 19.54; N, 3.62.

$PdCl_2[C_3(t\text{-}Bu)_2][(CH_3)_2SO]$ (2f). This was obtained by stirring 1b (0.5 mmol) in DMSO(10 ml) for 2 h. To this solution was added 10 ml of ether, which afforded yellow crystals of 2f in 67 % yield: mp. 202°C (dec.); IR(KBr): 2975, 1478, 1402, 1376, 1345, 1332, 1238, 1190, 1030 cm^{-1}; PMR($CDCl_3$): δ 2.90(s, SCH_3), 1.48 ppm(s, t-Bu).

Anal. calcd for $C_{13}H_{24}Cl_2OSPd$: C, 38.46; H, 5.97; Cl, 17.49.
Found : C, 38.02; H, 5.78; Cl, 17.68.

Trans-$PdCl(C_3R_2)(PR'_3)_2 \cdot ClO_4$ (3a - c). A solution of 2a - c(0.1 mmol) in methylene chloride(10 ml) was cooled to -60°C. To this was added phosphine(0.1 mmol) under stirring. After stirring for another 2 h at room temperature, the reaction mixture was washed with 0.1 % $HClO_4$ aq. and extracted with methylene chloride. The solvent was removed and residual materials was chromatographed on silica gel with methylene chloride/ether (3:1), affording colorless crystals of 3a - c.

Trans-$PdCl[C_3(i\text{-}Pr)_2](n\text{-}Bu_3P)_2 \cdot ClO_4$ (3a) - Recrystallization

from hexane/acetone gave colorless crystals of 3a in 92 % yield: mp. 151°C; IR(KBr): 2960, 1778, 1468, 1427, 1382, 1356, 1275, 1158, 1090, 903, 800, 726, 621 cm^{-1}; PMR($CDCl_3$): δ 4.08(sep, CH), 1.60(d, CH_3), 0.70 - 2.30 ppm(m, n-Bu); ^{13}C NMR($CDCl_3$): δ 205.4(C_{ring}-Pd), 198.7 ($\underline{C}_{ring}$-C), 29.1(CH), 19.3(CH_3), 13.8 - 26.6 ppm(n-Bu); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 244(2785), 284 nm(2624).

Anal. calcd for $C_{33}H_{68}Cl_2O_4P_2Pd$: C, 51.60; H, 8.92; Cl, 9.23.
Found : C, 51.52; H, 8.99; Cl, 9.25.

Trans-$PdCl[C_3(t\text{-}Bu)_2](n\text{-}Bu_3P)_2 \cdot ClO_4$ (3b) - Recrystallization from hexane/acetone afforded colorless crystals of 3b in 68 % yield: mp. 164°C; IR(KBr): 2960, 1775, 1466, 1377, 1333, 1207, 1172, 1090, 905, 725, 622 cm^{-1}; PMR($CDCl_3$): δ 1.55(s, CH_3), 0.70 2.00 ppm (m, n-Bu); ^{13}C NMR($CDCl_3$): δ 205.8(C_{ring}-Pd), 199.7($\underline{C}_{ring}$-C), 34.8($\underline{C}$-CH_3), 27.6(CH_3), 13.6 - 26.5 ppm(n-Bu); UV(CH_2Cl_2): $\lambda_{max}(\varepsilon_{max})$ 248(8820), 286 nm(8190).

Anal. calcd for $C_{35}H_{72}Cl_2O_4P_2Pd$: C, 52.80; H, 9.11; Cl, 8.91.
Found : C, 52.87; H, 9.45; Cl, 8.99.

Trans-$PdCl(C_3Ph_2)(n\text{-}Bu_3P)_2 \cdot ClO_4$ (3c) - Recrystallization from methylene chloride/ether afforded colorless crystals of 3c in 60 % yield: mp. 135°C; IR(KBr): 3060, 2965, 1788, 1598, 1463, 1336, 1320, 1303, 1090, 771, 688, 622 cm^{-1}; PMR($CDCl_3$): δ 8.47 - 8.70, 7.80 - 8.10 (m, Ph), 0.70 - 2.30 ppm(m, n-Bu); ^{13}C NMR($CDCl_3$): δ 195.2(C_{ring}-Pd), 176.0($\underline{C}_{ring}$-Ph), 137.8, 133.4, 130.9, 120.8(Ph), 13.6 - 26.7 ppm(n-Bu).

Anal. calcd for $C_{39}H_{64}Cl_2O_4P_2Pd$: C, 56.02; H, 7.71; Cl, 8.48.

Found : C, 55.86; H, 7.87; Cl; 8.62.

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CHAPTER 5

SYNTHESES AND PROPERTIES OF CYCLOPROPENYLIDENE (Cr, Mo, W) COMPLEXES - DESULFURIZATION AND DESELENIZATION REACTIONS OF CYCLOPROPENETHIONES AND CYCLOPROPENESELONES

SUMMARY

A variety of chromium, molybdenum, and tungsten complexes of cyclopropenylidenes, $(RR'C_3)M(CO)_5$ (R= Me_2N, i-Pr_2N, t-BuS, Ph; R'= Me_2N, i-Pr_2N, t-BuS, Ph; M= Cr, Mo, W) have been synthesized by desulfurization and deselenization reactions of cyclopropenethiones and cyclopropeneselones. These reactions seem to proceed via $(RR'C_3)XM(CO)_5$ (R= Me_2N, i-Pr_2N, t-BuS, Ph; R'= Me_2N, i-Pr_2N, t-BuS, Ph; M= Cr, Mo, W; X= S, Se).

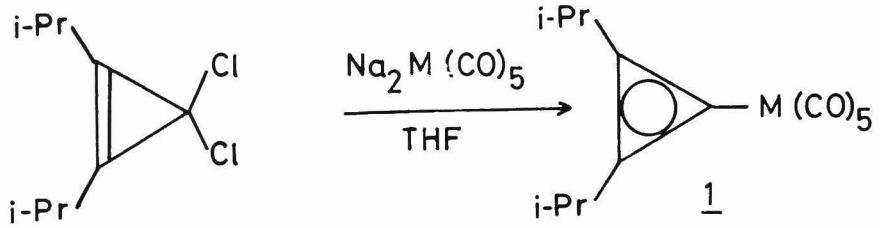
INTRODUCTION

As was described in Chapters 2 and 4, square planar type transition metal complexes of several cyclopropenylidenes can be synthesized through two types of synthetic routes which involve oxidative addition of halocyclopropenium cations or dihalocyclopropenes to zerovalent metal and direct metal-metal exchange reaction between cyclopropenylidene lithium and appropriate transition metal complexes. Unfortunately, bisthiocyclopropenylidene transition metal complexes cannot be synthesized by above methods, because of a probable strong affinity of sulfur to transition metals, which is resistant to these reactions. However, such affinity may be utilized for the syntheses of some cyclopropenylidene complexes. This idea has led to the successful desulfurization of cyclopropenethiones to cyclopropenylidene complexes.

In this chapter are described the syntheses of diverse cyclopropenylidene pentacarbonyl complexes. So far pentacarbonyl complex of bisphenylcyclopropenylidene, $(Ph_2C_3)M(CO)_5$, has been the only example of this type of complexes. It was prepared from 1,2-bisphenyl-3,3-dichlorocyclopropene and $Na_2M(CO)_5$.[1)]

RESULTS AND DISCUSSION

Öfele reported that nucleophilic attack of $Na_2Cr(CO)_5$ to 1,2-bisphenyl-3,3-dichlorocyclopropene afforded pentacarbonyl chromium complex of bisphenylcyclopropenylidene.[1)] By a quite similar manner pentacarbonyl chromium and -molybdenum complexes of bis(i-propyl)cyclopropenylidene can be obtained. These complexes are stable below their melting points



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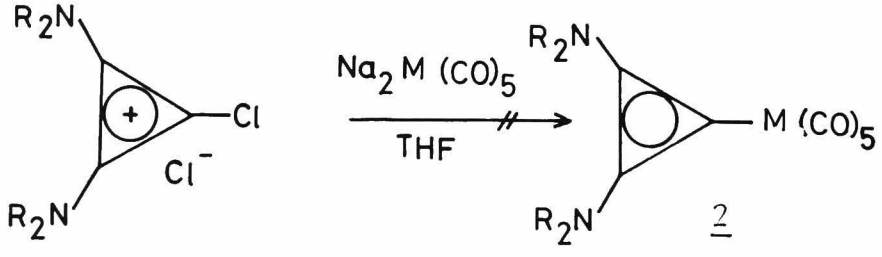
M		Yield
Cr	1a	19 %
Mo	1b	21 %

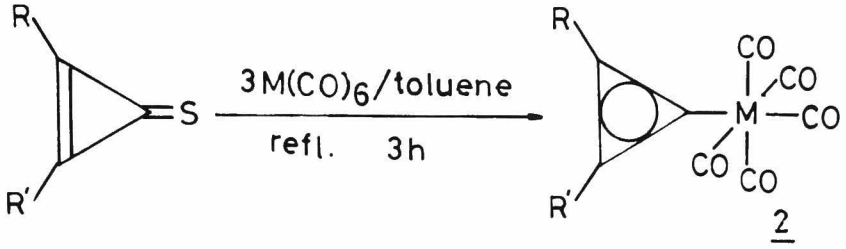
but gradually decompose at higher temperatures.

However, above method cannot be applicable to the syntheses of bisaminocyclopropenylidene complexes. Nucleophilic attack of $Na_2M(CO)_5$ on bisaminocyclopropenium chloride does not occur because of decreased positive charge on the C-3 ring owing to the strong electron release from two peripheral amino groups.



2

Therefore the present desulfurization reaction of cyclopropenethiones is a very useful method for the syntheses of bisaminocyclopropenylidene complexes.

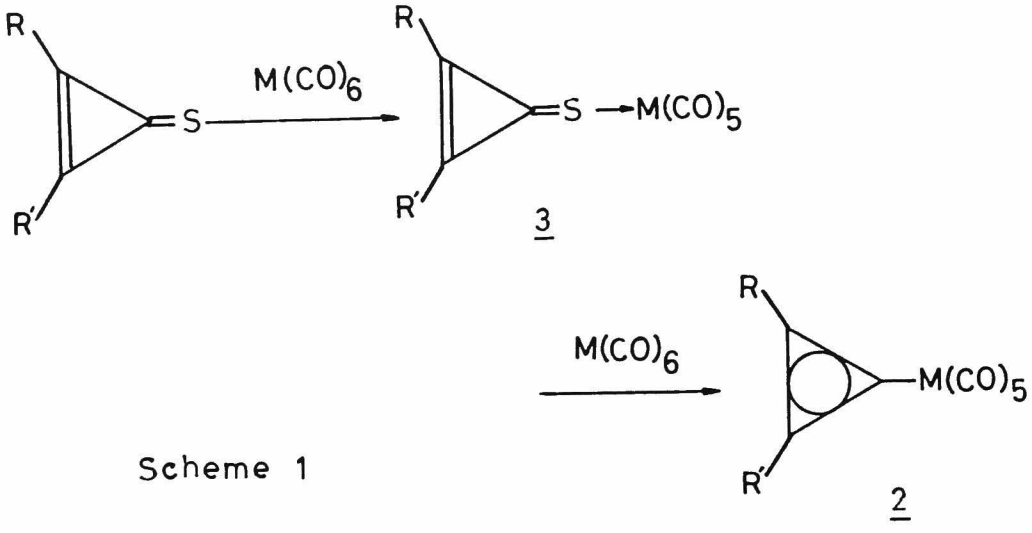


M ; Cr, Mo, W
R ; Me_2N, i-Pr_2N
R' ; Me_2N, i-Pr_2N, t-BuS, Ph

Table 1 Yields and characteristics of the complexes, 2a - j.

	R	R'	M*	Yield(%)	Mp.(°C)	Color
2a	Me_2N	Me_2N	Cr	47	154	pale yellow
2b	Me_2N	Me_2N	Mo	70	146	pale yellow
2c	Me_2N	Me_2N	W	58	152	pale yellow
2d	i-Pr_2N	i-Pr_2N	Cr	64	135	pale yellow
2e	i-Pr_2N	i-Pr_2N	Mo	71	134	pale yellow
2f	i-Pr_2N	i-Pr_2N	W	66	157	pale yellow
2g	Me_2N	t-BuS	Cr	29	99	pale yellow
2h	Me_2N	t-BuS	Mo	31	112	pale orange
2i	i-Pr_2N	Ph	Cr	30	130	pale yellow
2j	i-Pr_2N	Ph	Mo	25	126	pale orange

*) Three molar amounts of $M(CO)_6$ were used for each cyclopropene-thione.



Scheme 1

Bis(dimethylamino)cyclopropenethiones and three molar equiv. of $Cr(CO)_6$ were heated in refluxing toluene for 4 h under an atmosphere of argon to afford the corresponding bis(dimethylamino)cyclopropenylidene complex 2a in relatively high yields (Table 1). Molybdenum and tungsten complexes 2b and c are also obtainable by similar method. This desufurization reaction is useful for the preparation of bis(di-i-propylamino)-cyclopropenylidene complexes 2d - f. Furthermore this reaction is applicable to the preparation of monoaminocyclopropenylidene complexes. Chromium and molybdenum complexes of dimethylamino-t-butylthio- and di(i-propylamino)-phenylcyclopropenylidene 2g - j were synthesized from corresponding cyclopropenethiones (Table 1).

When cyclopropenethiones and equimolar amounts of $M(CO)_6$ were treated at lower temperatures than that described above, 2 could not be obtained but the sulfur ligated complexes 3 were obtained. The yields of 3 are shown in Table 2 together with the reaction conditions.

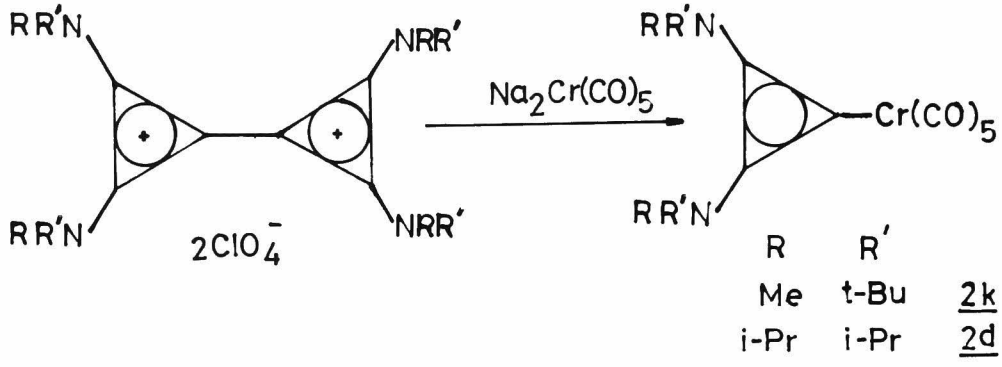
Table 2 Reaction conditions and yields of the complexes, 3a - i.

	R	R'	M*	Temp(°C)	Time(h)	Yield(%)	Mp.(dec.°C)
3a	i-Pr_2N	i-Pr_2N	Cr	100	1	83	105
3b	i-Pr_2N	i-Pr_2N	Mo	100	1	95	120
3c	i-Pr_2N	i-Pr_2N	W	100	1	92	155
3d	Me_2N	t-BuS	Cr	100	6	40	115
3e	Me_2N	t-BuS	Mo	100	4	41	113
3f	i-Pr_2N	Ph	Cr	100	6	62	118
3g	i-Pr_2N	Ph	Mo	100	4.5	51	110
3h	t-BuS	t-BuS	Cr	108	3	15	150
3i	t-BuS	t-BuS	Mo	108	1.5	12	126

*) Equimolar amounts of $M(CO)_6$ was used for cyclopropenethiones 3a - g and three molar amounts of $M(CO)_6$ for 3h and 3i.

The complex 3a on reaction with excess amounts of $Mo(CO)_6$ in refluxing toluene afforded 2e in high yields. However heating 3a alone in refluxing toluene gave meager amounts of 2e. In addition bis(di-i-propylamino)cyclopropenethione and equimolar amounts of $Mo(CO)_6$ gave 2e in very low yields when heated in refluxing toluene. These facts suggest that the reaction from cyclopropenethione to cyclopropenylidene complex 2 proceeds via 3 as shown in Scheme 1.

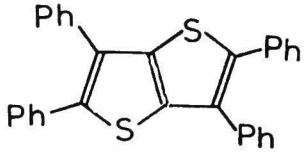
Bisaminocyclopropenylidene complex was also prepared by cleaving C - C bond of tetraaminotriafulvalene dication with $Na_2M(CO)_5$. Bis-(t-butyl-methylamino)cyclopropenylidene chromium complex 2k was obtained in 44 % yield from tetra(t-butyl-methylamino)triafulvalene dication and excess amounts of $Na_2Cr(CO)_5$.



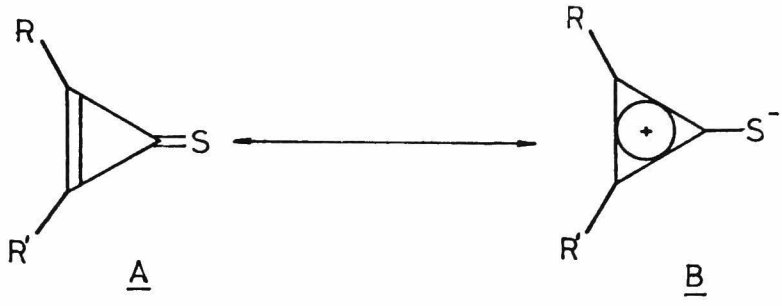
R	R'	
Me	t-Bu	2k
i-Pr	i-Pr	2d

Thus aminocyclopropenethiones reacted with $M(CO)_6$ to afford the corresponding aminocyclopropenylidene complexes, but the cyclopropenethiones which have no strong electron donating substitutents on the C-3 rings, such as bisphenylcyclopropenethione, did not give corresponding complex in any conditions examined. The sole detectable product was tetraphenylthienothiophene 4 when bisphenylcyclopropenethione was treated with $Cr(CO)_6$ in some reaction conditions. Schoenberg and his co-workers prepared 4 by irradiation of bisphenylcyclopropenethione.[2] However such a dimerization reaction catalyzed by transition metals and not by irradiation is the first case.

Bis(t-butylthio)cyclopropenethione also did not afford bis(t-butylthio)cyclopropenylidene complex but gave only 3h and 3i by reaction in diverse conditions. Higher reaction temperatures resulted in decomposition of the reactants. Such difference in reactivity can be correlated

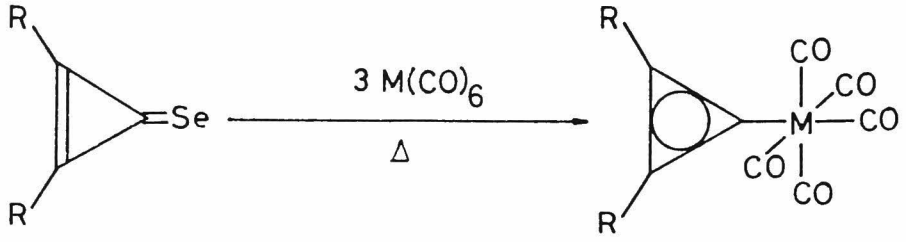


4

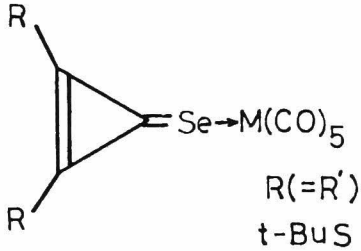


with the polarizability of C=S bonds, that is, loosening of C=S bonds of cyclopropenethiones. Electron donating amino groups stabilize the polarized form B more than phenyl and alkylthio groups do. Starting materials which have more loosened C=S bonds would be more favorable to such a reaction as that from cyclopropenethiones to cyclopropenylidene complexes which involve cleavage of the C=S bond.

Bisthiocyclopropenylidene complexes 5a and b could be synthesized more easily and more successfully through deselenization reaction of bisthiocyclopropeneselone. This is undoubtedly based on the more looseness of C - Se bonds compared to C - S bonds. Bis(t-butylthio)cyclopropeneselone, when heated with three molar amounts of $M(CO)_6$, afforded bis(t-butylthio)cyclopropenylidene complexes, 5a and b in reaction conditions as shown in Table 3. Bisphenylcyclopropenylidene complex 6a was also obtained from bisphenylcyclopropeneselone and $Mo(CO)_6$. These reaction might proceed via 7, similar to the reaction path from bisaminocyclopropenethione to 2. Bis(t-butylthio)cyclopropeneselone and equimolar amounts of $M(CO)_6$ heated at 90 - 100°C in toluene, afforded the corresponding complexes, 7a and b. These complexes, treated with excess



R(=R')	M	
t-BuS	Cr	5a
t-BuS	Mo	5b
Ph	Mo	6b



7

R(=R')	M	
t-BuS	Cr	7a
t-BuS	Mo	7b

amounts of $M(CO)_6$ in the same conditions where 5a and b were obtained from bis(t-butylthio)cyclopropeneselone and $M(CO)_6$ gave 5a and b.

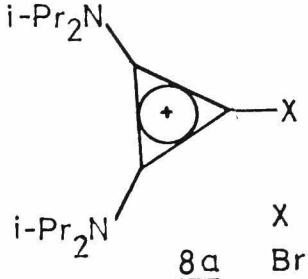
Bisaminocyclopropenylidene complexes were obtained from bisaminocyclopropeneselone and $M(CO)_6$ in higher yields at milder conditions than the case from bisaminocyclopropenethione and $M(CO)_6$. For instance, bis(di-i-propylamino)cyclopropeneselone, treated with $Cr(CO)_6$ in refluxing benzene, afforded 2d in 94 % yield.

The complexes 2, 5, and 6 are all stable at room temperature in atmosphere. The appreciable stability of molybdenum complexes is noteworthy in comparison with that of general Wanzlic type carbene complexes, such as $Ph(MeO)CMo(CO)_5$.[3)]

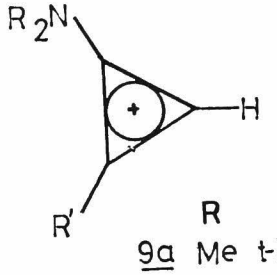
Table 3 Reaction conditions and yields about the complexes, 5a, b, 6b, 2d, and f.

	R(=R')	M	Temp.(°C)	Time(h)	Solv.	Yield(%)	Mp.(°C)
5a	t-BuS	Cr	105	5	toluene	5.1	134
5b	t-BuS	Mo	100	1.5	toluene	6.5	151
6b	Ph	Mo	refl.	1	benzene	23	180
2d	i-Pr_2N	Cr	refl.	2	benzene	94	135
2f	i-Pr_2N	Mo	refl.	2	benzene	88	134

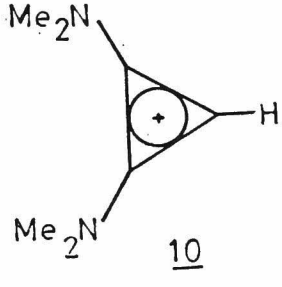
Bisaminocyclopropenylidene complex 2 shows some resistance to alkaline hydrolysis. The complex 2d was not hydrolyzed in 3 N KOH methanolic solution after 4 days. When 2d was treated with bromine, bis(amino)bromocyclopropenium cation 8a was obtained. However, 2d was easily attacked by acids, such as dil. $HClO_4$, CH_3CO_2H, and even by $(HNEt_3)\cdot CH_3CO_2$ to afford bisaminocyclopropenium cation 8b. Similarly dimethylamino-t-butylthiocyclopropenylidene complex 2h and di-i-propylamino-phenylcyclopropenylidene complex 2j were able to be led to corresponding cyclopropenium cation 9a and b, respectively.



	X
8a	Br
8b	H



	R	R'
9a	Me	t-BuS
9b	i-Pr	Ph



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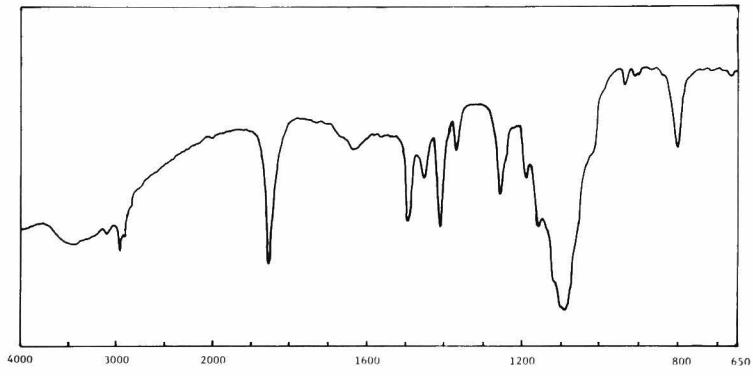


Fig. 1. Infrared spectrum of 9a.

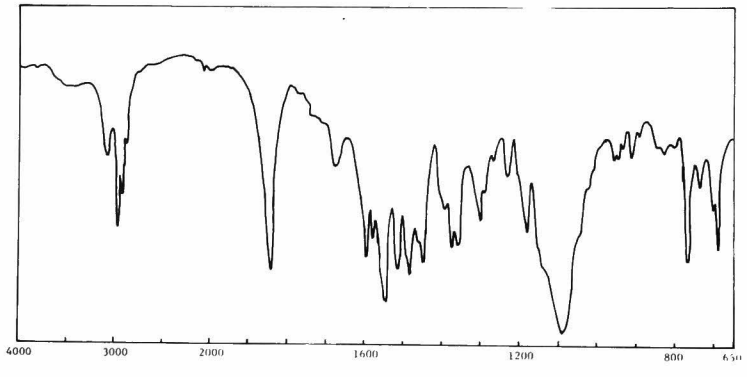
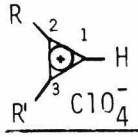


Fig. 2. Infrared spectrum of 9b.

So far, there has been no appropriate method of preparation for such monoaminocyclopropenium cations. These cation are stable in crystalline state but gradually decompose in organic solvent even at room temperature. PMR and ^{13}C-NMR parameters for 9a and b are shown in Table 4. The large $J(C_{ring}-H)$ in 9a and b indicates sp hybridization

Table 4 NMR parameter of several cyclopropenium cations.

 ClO_4^-	R	R'	Ring Carbon C_1	Ring Carbon $C_{2,3}$	J_{C-H}(Hz)	Ring Proton δ H
9a	Me_2N	t-BuS	125.3	146.9, 145.7	251	9.04
9b	i-Pr_2N	Ph	131.2	144.5, 144.3	248	9.63
10	Me_2N	Me_2N	96.1	138.1	242	7.02
8b	i-Pr_2N	i-Pr_2N	99.1	133.8	242	7.40
11[5]	Ph	Ph	155.6	164.1	253	10.7

of C - H bond.[4] In addition values of $J(C_{ring}- H)$ and all chemical shifts for 9a and b are between those of bisaminocyclopropenium cation 10 and bisphenylcyclopropenium cation 11, suggesting that the charge density on C-3 rings of 9a and b are intermediate between those of

Table 5 Mass fragments of some cyclopropenylidene complexes.

	2a		5a		6a[1]	
	M/e	I_{rel}	M/e	I_{rel}	M/e	I_{rel}
$LCr(CO)_5^+$	316	11	406	69	382	9.6
$LCr(CO)_4^+$	288	5	378	11	354	0.2
$LCr(CO)_3^+$	260	5	350	17	326	4
$LCr(CO)_2^+$	232	7	322	16	298	9.7
$LCr(CO)^+$	204	21	294	35	270	17
LCr^+	176	100	266	100	242	100

L = $RR'C_3$

10 and 11.

The mass spectrum of 2a exhibits molecular ion peak at m/e = 316, indicating this complex to be monomeric. Other fragment ions are listed in Table 5. The fragmentation patterns of 2a, 5a, and 6a[1] are similar to one another and these are also analogous to that of Wanzlic type carbene complex, pentacarbonyl(N,N'-dimethylimidazoiline-2-ylidene) chromium 12.[6]

In the infrared spectra, all cyclopropenylidene complexes 1, 2, 5, and 6 and related compounds 3 and 7 show two or three CO stretching vibrational bands characteristic of C_{4v} pentacarbonyl complexes[7] in the rigion of 1910 - 2100 cm^{-1}. On the other hand, bisaminocyclopropenylidene complexes 2a - f exhibit two characteristic bands at 1830 - 1900 and 1470 - 1540 cm^{-1}(Table 6). The former is assigned to the C-3 core deformation and the latter to the C_{ring}- N bond stretching.

Table 6
The ring deformation and C_{ring}-N stretching absorption bands on 2a-f and 10.

	$\nu_{\Delta}(cm^{-1})$	$\nu_{C-N}(cm^{-1})$
2a	1899	1534
2b	1893	1534
2c	1892	1530
2d	1834	1475
2e	1829	1478
2f	1829	1479
10	1916	1615

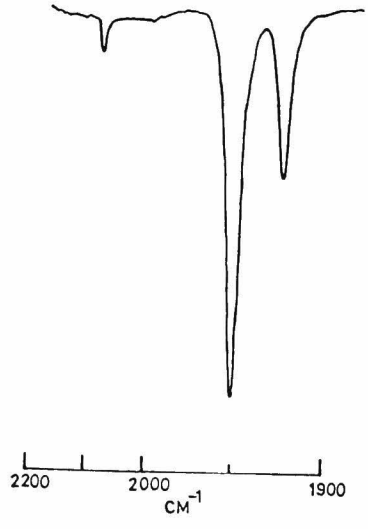


Fig. 3. CO stretching ir bands of 3i in hexane.

Both absorption bands are at lower frequencies compared to that of bisaminocyclopropenium cation 10. These trends are seen in the case of bisaminocyclopropenylidene palladium complexes[8,9] (see Chapter 2).

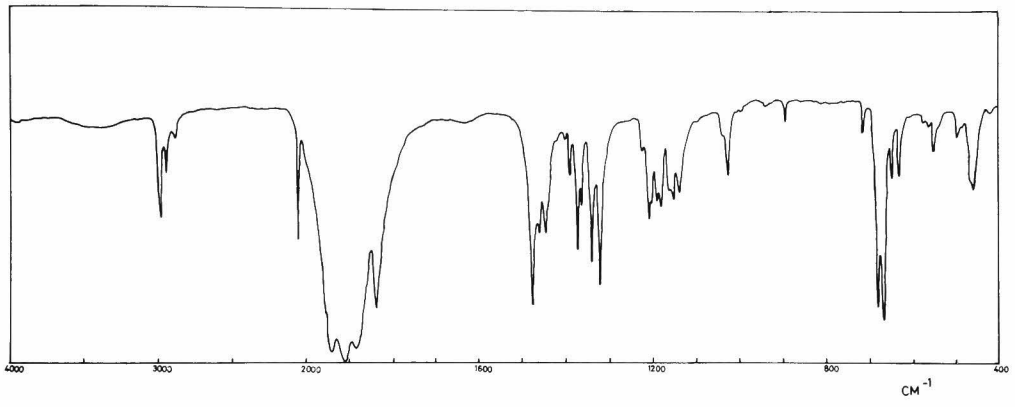


Fig. 4. Infrared spectrum of 2d.

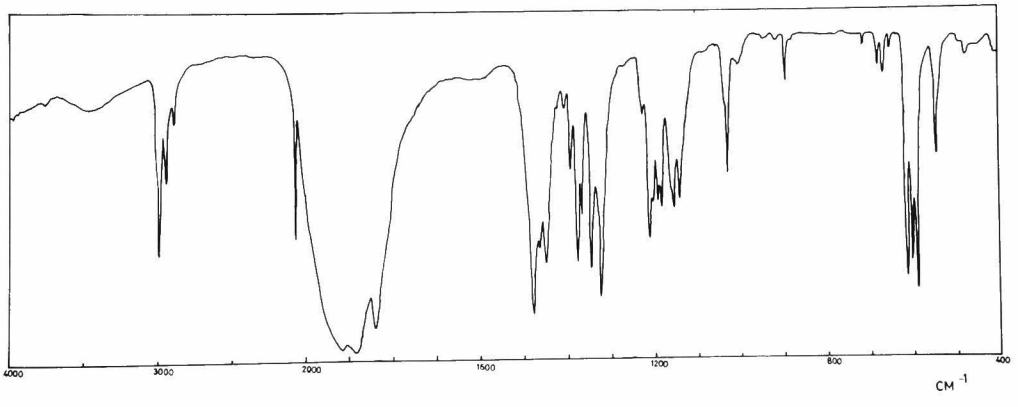


Fig. 5. Infrared spectrum of 2e.

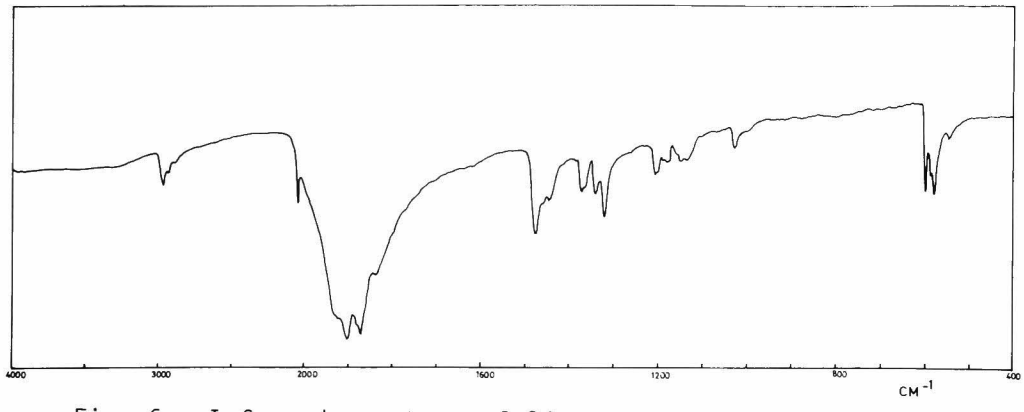


Fig. 6. Infrared spectrum of 2f.

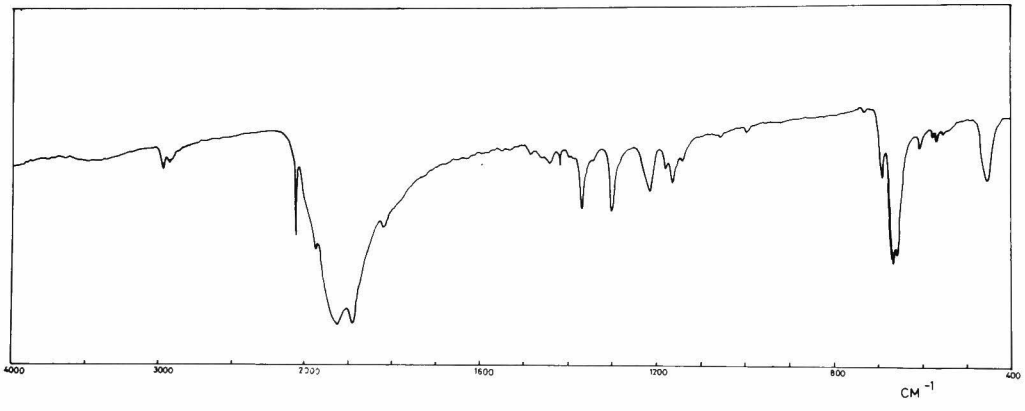


Fig. 7. Infrared spectrum of 2g.

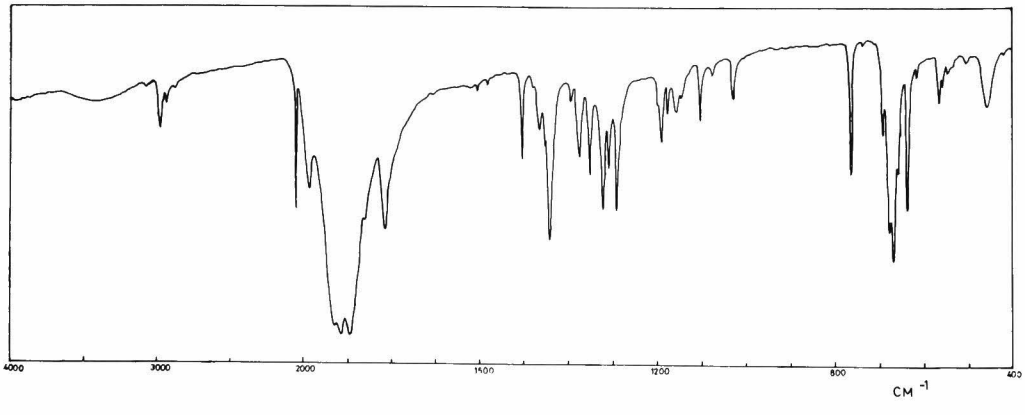


Fig. 8. Infrared spectrum of 2i.

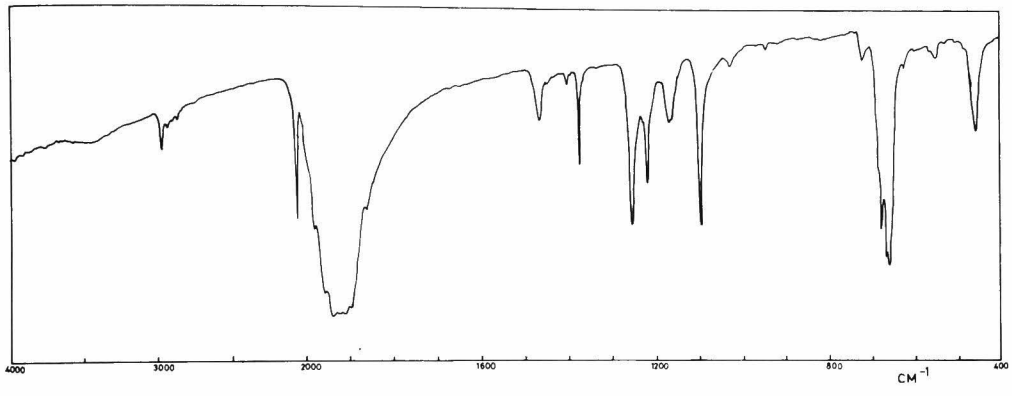


Fig. 9. Infrared spectrum of 5a.

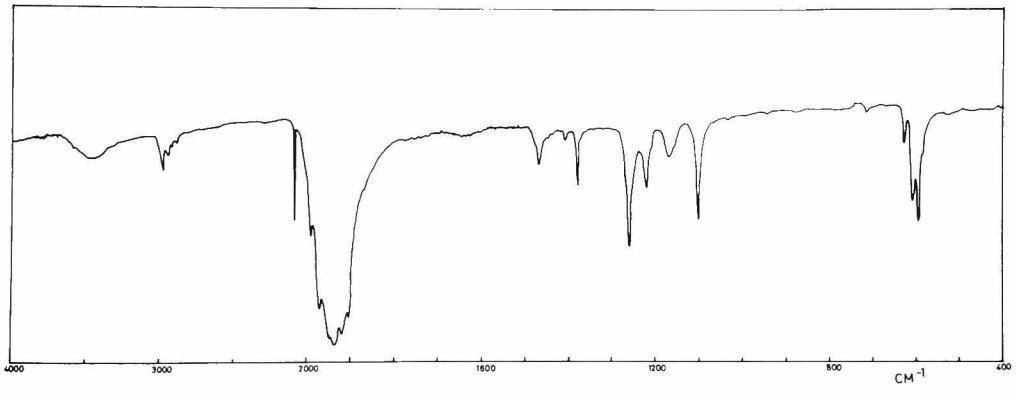


Fig. 10. Infrared spectrum of 5b.

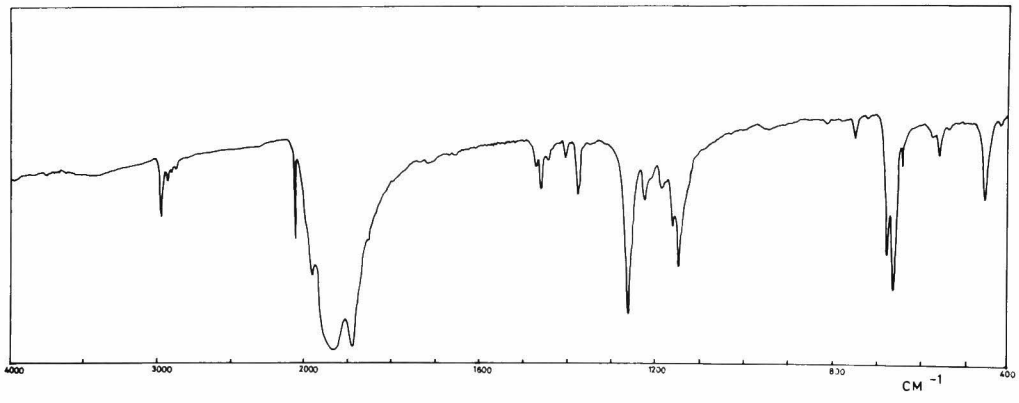


Fig. 11. Infrared spectrum of 3h.

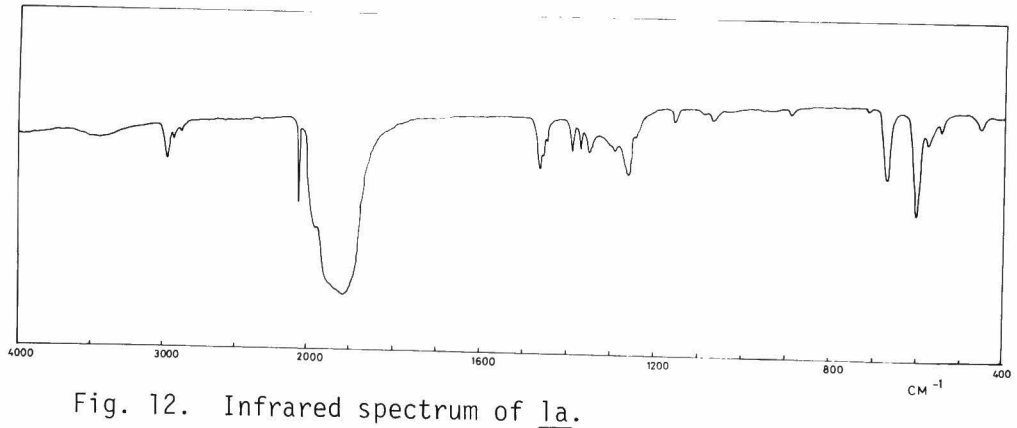


Fig. 12. Infrared spectrum of 1a.

EXPERIMENTAL

Synthesis of $(i\text{-}Pr_2C_3)M(CO)_5$ (1a, b). To bis-i-propylcyclopropenone (2.0 mmol) in 5 ml of dry CH_2Cl_2 was added 0.22 ml of $(COCl)_2$. After half an hour the solvent was removed under reduced pressure to afford a sirupy oil of 1,2-bis-i-propyl-3,3-dichlorocyclopropene. This was dissolved into 10 ml of dry deoxygenated THF and cooled in a dryice-acetone bath. To this was added 20 ml of 0.1 M $Na_2M(CO)_5$/THF solution which was prepared by the usual manner[10]. After 30 min the solution was allowed to warm up to room temperature and stirred for additional one hour. The reaction mixture was evaporated and the residue was chromatographed on silica gel with benzene. Removal of $M(CO)_6$ under reduced pressure at 60°C and subsequent crystallization from hexane at -70°C gave fine crystals of 1a and b in 19 and 23 % yields, respectively.

$(i\text{-}Pr_2C_3)Cr(CO)_5$ (1a) - Pale yellow crystals: mp. 18°C; IR(KBr): 2975, 2070 - 1850, 1463, 1385, 1367, 1348, 1293, 1260, 1153, 1060, 884, 708, 660 cm^{-1}; PMR($CDCl_3$): δ 3.36(sep, CH), 1.43 ppm(d, CH_3); ^{13}C NMR ($CDCl_3$): δ 236.3(C_{ring}- Cr), 222.4(trans CO), 218.3(cis CO), 200.1 (C_{ring}- C), 29.0(CH), 19.9 ppm(CH_3); UV(CH_3CN): $\lambda_{max}(\varepsilon_{max})$ 245(3200), 329 nm(770).

Anal. calcd for $C_{14}H_{14}CrO_5$: C, 53.51; H, 4.49.
Found : C, 53.51; H, 4.64.

$(i\text{-}Pr_2C_3)Mo(CO)_5$ (1b) - Pale brown crystals: mp. 23°C; IR(KBr): 2975, 2070 - 1850, 1470, 1392, 1372, 1351, 1296, 1265, 670, 605 cm^{-1}; PMR($CDCl_3$): δ 3.37(sep, CH), 1.43 ppm(d, CH_3); ^{13}C NMR($CDCl_3$): δ 227.5 (C_{ring}- Mo), 214.5(trans CO), 206.9(cis CO), 199.1(C_{ring}- C), 29.1(CH),

19.7 ppm(CH_3); UV(CH_3CN): $\lambda_{max}(\varepsilon_{max})$ 247(32800), 285(8660), 331 nm (7910).

Anal. calcd for $C_{14}H_{14}MoO_5$: C, 46.94; H, 3.94.
Found : C, 47.02; H, 3.90.

$(Ph_2C_3)M(CO)_5$ (6a, b). This was prepared by the method reported by Öfele.[1)]

$(Ph_2C_3)Cr(CO)_5$ (6a) - Orange crystals: mp. 199°C; IR(KBr): 3065, 2055 - 1850, 1351, 1322, 1303, 1274, 1169, 765, 683, 658, 632, 599, 462 cm^{-1}; PMR($CDCl_3$): δ 8.30 - 7.70 ppm(m, Ph); ^{13}C NMR($CDCl_3$): δ 228.6 (C_{ring}- Cr), 224.0(tran CO), 217.5(cis CO), 181.8(C_{ring}-C), 124.0, 132.2, 129.7, 134.5 ppm(Ph); UV(CH_3CN): $\lambda_{max}(\varepsilon_{max})$ 218(9900), 227(9900), 280(9800), 288(9800), 298(9900), 315(sh, 4700), 368 nm(5300).

$(Ph_2C_3)Cr(CO)_5$ (6b) - Yellow crystals: mp. 180°C(dec.); IR(KBr): 3065, 2060 - 1850, 1348, 1322, 1308, 1275, 1167, 763, 683, 665, 597, 575, 544, 499 cm^{-1}; PMR($CDCl_3$): δ 8.30 - 7.70 ppm(m, Ph); ^{13}C NMR($CDCl_3$): δ 220.2(C_{ring}-Mo), 214.0(trans CO), 206(cis CO), 181.2(C_{ring}-C), 124.7, 132.5, 130.3, 135.2 ppm(Ph); UV(CH_3CN): $\lambda_{max}(\varepsilon_{max})$ 344(9310), 368 nm (10880).

Synthesis of $(RR'C_3)M(CO)_5$ (2a - j) by Reaction of Cyclopropenethione with $M(CO)_6$. A mixture of cyclopropenethione(1 mmol) and $M(CO)_6$(3 mmol) in freshly distilled toluene(30 ml) was refluxed in reaction vessel under argon. After 3 - 6 h, the solvent and excess $M(CO)_6$ were removed under reduced pressure and residual materials were chromatographed on silica gel with benzene. Crystallization from

methanol gave pure crystals of 2a - j.

$[(Me_2N)_2C_3]Cr(CO)_5$ (2a) Pale yellow crystals: mp. 154°C; IR(KBr) : 2940, 2060 - 1800, 1534, 1415, 1407, 1352, 1218, 1199, 996, 786, 699, 668, 655, 641, 456 cm^{-1}; PMR($CDCl_3$): δ 3.20 ppm(s, CH_3); ^{13}C NMR($CDCl_3$) : δ 224.3(trans CO), 219.2(cis CO), 157.7(C_{ring}- N), 152.6(C_{ring}- Cr), 41.0 ppm(CH_3); UV(CH_3CN): $\lambda_{max}(\varepsilon_{max})$ 249(27000), 349 nm(3400).

Anal calcd for $C_{12}H_{12}CrN_2O_5$: C, 45.58; H, 3.83; N, 8.86.

Found : C, 45.29; H, 3.81; N, 8.61.

$[(Me_2N)_2C_3]Mo(CO)_5$ (2b) - Pale yellow crystals: mp. 146°C; IR (KBr): 2940, 2070 1800, 1534, 1399, 1350, 1321, 1188, 997, 607, 592, 578 cm^{-1}; PMR($CDCl_3$): δ 3.12 ppm(s, CH_3); ^{13}C NMR($CDCl_3$): δ 213.6(trans CO), 207.9(cis CO), 156.5(C_{ring}- N), 146.2(C_{ring} - Mo), 38.8, 42.7 ppm (CH_3); UV(CH_3CN): $\lambda_{max}(\varepsilon_{max})$ 228(33300), 247(39600), 289(sh, 12200), 331(3514), 364 nm(3153).

Anal calcd for $C_{12}H_{12}MoN_2O_5$: C, 40.02; H, 3.36; N, 7.78.

Found : C, 39.82; H, 3.23; N, 7.51.

$[(Me_2N)_2C_3]W(CO)_5$ (2c) - Pale yellow crystals: mp. 157°C; IR(KBr) : 2940, 2065 - 1800, 1530, 1398, 1352, 599, 585, 574 cm^{-1}; PMR($CDCl_3$): δ 3.16 ppm(s, CH_3); ^{13}C NMR($CDCl_3$): δ 203.9(trans CO), 199.2(cis CO), 155.3(C_{ring}- N), 136.0(C_{ring}- W), 41.1 ppm(CH_3).

Anal calcd for $C_{12}H_{12}N_2O_5W$: C, 32.17; H, 2.70; N, 6.25.

Found : C, 31.89; H, 2.63; N, 6.11.

$[(i\text{-}Pr_2N)_2C_3]Cr(CO)_5$ (2d) - Pale yellow crystals: mp. 135°C; IR (KBr): 2970, 2060 - 1800, 1475, 1444, 1369, 1336, 1316, 1204, 1185, 1177, 1146, 1134, 1023, 674, 560, 641, 449 cm^{-1}; PMR($CDCl_3$): δ 4.28

(sep, CH), 1.37 ppm(d, CH_3); ^{13}C NMR($CDCl_3$): δ 222.8(trans CO), 218.8 (cis CO), 154.5(C_{ring}- N), 152.2(C_{ring}- Cr), 49.9(CH), 22.1 ppm(CH_3).

Anal. calcd for $C_{20}H_{28}CrN_2O_5$: C, 56.07; H, 6.59; N, 6.53.

Found : C, 55.89; H, 6.68; N, 6.29.

$[(i\text{-}Pr_2N)_2C_3]Mo(CO)_5$ (2e) - Pale yellow crystals: mp. 146°C; IR (KBr): 2975, 2060 - 1800, 1478, 1446, 1371, 1340, 1322, 1208, 1188, 1180, 1150, 1037, 1027, 608, 598, 588, 541 cm^{-1}; PMR($CDCl_3$): δ 4.24 (sep, CH), 1.36 ppm(d, CH_3); ^{13}C NMR($CDCl_3$): δ 212.5(trans CO), 207.2 (cis CO), 153.2(C_{ring}- N), 147.9(C_{ring}- Mo), 49.6(CH), 29.1 ppm(CH_3).

Anal. calcd for $C_{20}H_{28}MoN_2O_5$: C, 50.85; H, 5.97; N, 5.93.

Found : C, 50.84; H, 6.03; N, 5.90.

$[(i\text{-}Pr_2N)_2C_3]W(CO)_5$ (2f) - Pale yellow crystals: mp. 157°C; IR (KBr): 2970, 2060 - 1800, 1479, 1445, 1372, 1364, 1341, 1322, 1206, 1181, 1151, 1137, 1027, 600, 581, 545 cm^{-1}; PMR($CDCl_3$): δ 4.19(sep, CH), 1.36 ppm(d, CH_3); ^{13}C NMR($CDCl_3$): δ 202.5(trans CO), 199.2(cis CO), 151.9(C_{ring}- N), 136.4(C_{ring}- W), 50.1(CH), 22.1 ppm(CH_3); UV(CH_3CN): $\lambda_{max}(\varepsilon_{max})$ 229(123000), 256(sh, 33300), 288(sh, 17200), 370 nm(sh, 2471).

Anal. calcd for $C_{20}H_{28}N_2O_5W$: C, 42.88; H, 5.04; N, 5.00.

Found : C, 42.88; H, 5.29; N, 4.97.

$[Me_2N(t\text{-}BuS)C_3]Cr(CO)_5$ (2g) - Pale yellow crystals: mp. 99°C; IR(KBr): 2973, 2060 - 1800, 1368, 1298, 1214, 1162, 686, 661, 653, 606, 451 cm^{-1}; PMR($CDCl_3$): δ 3.34, 3.12(s, NCH_3), 1.73 ppm(s, CCH_3).

Anal. calcd for $C_{14}H_{15}CrNO_5S$: C, 46.54; H, 4.18; N, 3.89.
Found : C, 46.38; H, 4.32; N, 3.74.

$[Me_2N(t\text{-}BuS)C_3]Mo(CO)_6$ (2h) - Pale orange crystals: mp. 112°C; IR(KBr): 2790, 2065 - 1800, 1368, 1299, 1213, 1160, 619, 608, 594, 580, 568 cm^{-1}; PMR($CDCl_3$): δ 3.38, 3.14(s, NCH_3), 1.70 ppm(s, CCH_3).

Anal. calcd for $C_{14}H_{15}MoNO_5S$: C, 41.40; H, 3.73; N, 3.56.
Found : C, 41.13, H, 3.74; N, 3.40.

$[i\text{-}Pr_2N(Ph)C_3]Cr(CO)_5$ (2i) - Pale yellow crystals: mp. 130°C; IR (KBr): 3070, 2985, 2060 - 1800, 1503, 1445, 1379, 1352, 1321, 1309, 1291, 1167, 1102, 766, 670, 656, 638, 566, 459 cm^{-1}: PMR($CDCl_3$): δ 7.40 - 8.10(m, Ph), 4.97, 3.92(sep, CH), 1.43 ppm(d, CH_3).

Anal. calcd for $C_{20}H_{19}CrNO_5$: C, 59.26; H, 4.72; N, 3.46.
Found : C, 59.38; H, 5.00; N, 3.46.

$[i\text{-}Pr_2N(Ph)C_3]Mo(CO)_5$ (2j) - Pale orange crystals:mp. 126°C; IR (KBr): 3070, 2980, 2065 - 1800, 1502, 1444, 1376, 1351, 1324, 1309, 1290, 764, 690, 608, 584, 554 cm^{-1}; PMR($CDCl_3$): δ 7.14 8.19(m, Ph), 4.90, 3.94(sep, CH), 1.45, 1.44 ppm(d, CH_3).

Anal. calcd for $C_{20}H_{19}MoNO_5$: C, 53.46; H, 4.26; N, 3.12.
Found : C, 53.17; H, 4.49; N, 3.07.

Reaction of $[(Me(t\text{-}Bu)N)_2C_3]_2\cdot 2ClO_4$ with $Na_2Cr(CO)_5$. To a solution of $[(Me(t\text{-}Bu)N)_2C_3]_2\cdot 2ClO_4$(0.5 mmol) in 5 ml of dry deoxygenated THF was added slightly excess amounts of 0.1 M $Na_2Cr(CO)_5$/THF at -78°C. After warming up to room temperature, this was stirred overnight. The reaction mixture was evaporated and the residue was chromatographed on

silica gel with benzene, giving pale yellow crystals of 2k, in 44 % yield: mp. 151 °C; IR(KBr): 2970, 2060 1800, 1484, 1450, 1390, 1371, 1330, 1222, 1128, 1107, 680, 654, 455 cm^{-1}; PMR($CDCl_3$): 3.22(s, NCH_3), 1.50 ppm(s, CCH_3).

Anal. calcd for $C_{18}H_{24}CrN_2O_5$: C, 54.00; H, 6.04; N, 7.00.
Found : C, 54.02; H, 6.06; N, 6.76.

By quite similar procedure 2d was obtained from $[(i\text{-}Pr_2N)_2C_3]_2 \cdot 2ClO_4$(0.5 mmol) and slightly excess amounts of $Na_2Cr(CO)_5$ in 40 % yield.

Preparation of $(RR'C_3S)M(CO)_5$ (3a - i). A mixture of cyclopropenethione(1 mmol) and equimolar amounts of $M(CO)_6$ was stirred in dry toluene under reaction conditions, which are shown in Table 2. The solvent was removed and residue was chromatographed on silica gel with benzene/methylene chloride(5/1). Crystallization from benzene/hexane afforded the crystals of 3a - i.

$[(i\text{-}Pr_2N)_2C_3S]Cr(CO)_5$ (3a) - Green crystals: mp. 105°C(dec.); IR (KBr): 2975, 2065 1800, 1505, 1482, 1446, 1401, 1371, 1362, 1337, 1214, 1176, 1157, 1134, 1027, 668, 658 cm^{-1}; PMR($CDCl_3$): δ 4.00, 3.90 (sep, CH), 1.39 ppm(d, CH_3).

Anal. calcd for $C_{20}H_{28}CrN_2O_5S$: C, 52.16; H, 6.13; N, 6.08.
Found : C, 51.92; H, 6.38; N, 6.00.

$[(i\text{-}Pr_2N)_2C_3S]Mo(CO)_5$ (3b) Green crystals: mp. 120°C(dec.); IR (KBr): 2975, 2060 - 1800, 1508, 1454, 1402, 1373, 1364, 1340, 1216, 1178, 1159, 1130, 1019, 883, 730 cm^{-1}; PMR($CDCl_3$): δ 4.05, 3.94(sep, CH), 1.37 ppm(d, CH_3).

Anal. calcd for $C_{20}H_{28}MoN_2O_5S$: C, 47.62; H, 5.59; N, 5.55.

Found : C, 47.63; H, 5.62; N, 5.52.

$[(i\text{-}Pr_2N)_2C_3S]W(CO)_5$ (3c) - Yellow crystals: mp. 155°C(dec.); IR (KBr): 2975, 2065 - 1800, 1513, 1408, 1380, 1344, 1216, 1160, 1145, 1020, 596, 588, 573 cm^{-1}; PMR($CDCl_3$): δ 3.98(sep, CH), 1.39(d, CH_3).

Anal. calcd for $C_{20}H_{28}N_2O_5SW$: C, 40.55; H, 4.76; N, 4.73.

Found : C, 40.24; H, 4.98; N, 4.81.

$[Me_2N(t\text{-}BuS)C_3S]Cr(CO)_5$ (3d) - Yellow crystals: mp. 115°C; IR (KBr): 2975, 2060 - 1800, 1485, 1389, 1371, 1303, 1281, 1249, 1217, 1205, 1167, 1003, 785, 732, 668, 651, 550, 446 cm^{-1}; PMR($CDCl_3$): δ 3.15, 3.35(s, NCH_3), 1.65 ppm(s, CCH_3).

Anal. calcd for $C_{14}H_{15}CrNO_5S_2$: C, 42.74; H, 3.84; N, 3.56.

Found : C, 42.45; H, 4.12; N, 3.53.

$[Me_2N(t\text{-}BuS)C_3S]Mo(CO)_5$ (3e) - Green crystals: mp. 113°C(dec.); IR(KBr): 2970, 2065 - 1800, 1480, 1384, 1366, 1298, 1275, 1236, 1214, 1203, 1163, 1000, 805, 780 cm^{-1}; PMR($CDCl_3$): δ 3.16, 3.51(s, NCH_3), 1.66 ppm(s, CCH_3).

Anal. calcd for $C_{14}H_{15}MoNO_5S_2$: C, 38.45; H, 3.46; N, 3.20.

Found : C, 38.25; H, 3.18; N, 3.19.

$[i\text{-}Pr_2N(Ph)C_3S]Cr(CO)_5$ (3f) - Yellow crystals: mp. 118°C; IR(KBr): 3070, 2980, 2070 - 1820, 1515, 1466, 1448, 1378, 1355, 1321, 1310, 1183, 1160, 1020, 764, 664, 650 cm^{-1}; PMR($CDCl_3$): δ 7.40 - 7.90(m, Ph), 3.94, 4.10(sep, CH), 1.49, 1.39 ppm(d, CH_3).

Anal. calcd for $C_{20}H_{19}CrNO_5S$: C, 54.92; H, 4.38; N, 3.20.
Found : C, 54.95, H, 4.50; N, 3.29.

$[i\text{-}Pr_2N(Ph)C_3S]Mo(CO)_5$ (3g) Yellow crystals: mp. 110°C(dec.); IR(KBr): 3050, 2975, 2970 - 1800, 1509, 1467, 1459, 1351, 1319, 1309, 1178, 1154, 761, 713, 690, 606, 590 cm^{-1}: PMR($CDCl_3$): δ 7.40 - 7.90 (m, Ph), 3.96, 4.20(sep, CH), 1.49, 1.39 ppm(d, CH_3).

Anal. calcd for $C_{20}H_{19}MoNO_2S$: C, 49.90; H, 3.98; N, 2.91.
Found : C, 49.96; H, 4.05; N, 2.92.

$[(t\text{-}BuS)_2C_3S]Cr(CO)_5$ (3h) - Yellow crystals: mp. 150°C(dec.); IR (KBr): 2975, 2065 - 1800, 1458, 1378, 1261, 1224, 1161, 1148, 669, 656, 634, 550, 448 cm^{-1}; PMR($CDCl_3$): δ 1.64 ppm(s, CH_3).

Anal. calcd for $C_{16}H_{18}CrO_5S_3$: C, 43.83; H, 4.14.
Found : C, 43.84; H, 4.44.

$[(t\text{-}BuS)_2C_3S]Mo(CO)_5$ (3i) - Brownish yellow crystals: mp. 126°C (dec.); IR(KBr): 2975, 2070 - 1800, 1469, 1377, 1261, 1222, 1159, 1146, 606, 589 cm^{-1}; PMR($CDCl_3$): 1.62 ppm(s, CH_3).

Anal. calcd for $C_{16}H_{18}MoO_5S_3$: C, 39.83; H, 3.76.
Found : C, 39.65, H, 4.09.

Reaction of 3a with $Mo(CO)_6$ in Toluene. A mixture of 3a(1 mmol) and $Mo(CO)_6$(1.2 mmol) in freshly distilled toluene(10 ml) was heated for 1.5 h under reflux condition. The solvent and excess $Mo(CO)_6$ were removed under reduced pressure and the residue was chromatographed on silica gel with benzene. Crystallization from methanol afforded 2e in 80 % yield.

Reaction of Bisphenylcyclopropenethione with $Cr(CO)_6$. A mixture of bisphenylcyclopropenethione (1.5 mmol) and $Cr(CO)_6$ (4.5 mmol) in toluene(20 ml) was heated to 90°C under an argon atmosphere. After 4 h, the solvent was removed and residual materials were chromatographed on silica gel with methylene chloride. Crystallization from benzene afforded colorless crystals of 2,3,5,6-tetraphenylthieno[3,2-b]-thiophene in 23 % yield: mp. 277°C; IR(KBr): 3068, 1598, 1530, 1497, 1472, 1448, 1443, 1373, 1260, 1074, 1033, 913, 889, 764, 753, 701, 689 cm^{-1}; PMR(CD_2Cl_2): δ 7.25 - 7.50 ppm(m, Ph); Mass: M/e^+ 444.

Anal. calcd for $C_{30}H_{20}S_2$: C, 81.05; H, 4.53; S, 14.42.

Found : C, 81.05; H, 4.77; S, 14.44.

Synthesis of $(RR'C_3)M(CO)_5$(5a, b, 6b, 2d, f) from Cyclopropeneselone and $M(CO)_6$. A mixture of cyclopropeneselone(1 mmol) and $M(CO)_6$(3 mmol) in toluene(20 ml) was heated in a reaction vessel replaced by argon under the condition shown in Table 3. The reaction mixture was evapolated and, at the same time, excess $M(CO)_6$ was removed. Chromatographed on silica gel with benzene and crystallization from hexane afforded the crystals of 5a, b, 6b, 2d, and f.

$[(t\text{-}BuS)_2C_3]Cr(CO)_5$ (5a) - Pale brown crystals: mp. 134°C; IR (KBr): 2975, 2060 - 1800, 1463, 1373, 1255, 1218, 1162, 1099, 675, 666, 454 cm^{-1}; PMR($CDCl_3$): δ 1.65 ppm(s, CH_3); ^{13}C NMR($CDCl_3$): δ 223.2 (trans CO), 217.4(cis CO), 212.5(C_{ring}- Cr), 182.8(C_{ring}- S), 50.5 ($\underline{C}CH_3$), 31.8 ppm(CH_3); UV(CH_3CN): $\lambda_{max}(\varepsilon_{max})$ 236(19540), 319(sh, 10660), 332(11670), 347 nm(10150).

Anal. calcd for $C_{16}H_{18}CrO_5S_2$: C, 47.28; H, 4.46.

Found : C, 47.25; H, 4.45.

$[(t\text{-BuS})_2C_3]Mo(CO)_5$ (5b) Brown crystals: mp. 151°C; IR(KBr): 2975, 2080 - 1850, 1468, 1405, 1377, 1258, 1219, 1169, 1100, 712, 624, 605, 601, 598, 581 cm^{-1}; PMR($CDCl_3$): δ 1.63 ppm(s, CH_3); ^{13}C NMR($CDCl_3$): δ 21.7(trans CO), 205.7(cis CO), 205.4(C_{ring}- Mo), 181.2(C_{ring}- S), 50.8($\underline{C}CH_3$), 31.8 ppm(CH_3); UV(CH_3CN): $\lambda_{max}(\varepsilon_{max})$ 249(13820), 292(sh, 3279), 330(2925), 357 nm(sh, 2473).

Anal. calcd for $C_{16}H_{18}MoO_5S_2$: C, 42.67; H, 4.03.

Found : C, 42.68; H, 4.18.

Preparation of $(RR'C_3Se)M(CO)_5$ (7a, b). A mixture of bis-t-butylthiocyclopropeneselone(1 mmol) and equimolar amounts of $M(CO)_6$ in toluene(20 ml) was stirred at 90 - 100°C under an argon atmosphere. After 2 h, the solvent was removed and then, chromatographed on silica gel with benzene. Crystallization from hexane gave brown crystals of 7a and b.

$[(t\text{-BuS})_2C_3Se]Cr(CO)_5$ (7a) - Brown crystals: mp. 144°C(dec.); IR (KBr): 2975, 2060 - 1850, 1451, 1370, 1238, 1214, 1184, 1150, 670, 655 cm^{-1}; PMR($CDCl_3$): δ 1.63 ppm(s, CH_3).

Anal. calcd for $C_{16}H_{18}CrO_5S_2Se$: C, 39.59; H, 3.74.

Found : C, 39.59; H, 4.02.

$[(t\text{-Bu})_2C_3Se]Mo(CO)_5$ (7b) - Brown crystals: mp. 136°C(dec.); IR (KBr): 2975, 2070 - 1830, 1460, 1377, 1243, 1217, 1188, 1150, 610, 591 cm^{-1}; PMR($CDCl_3$): δ 1.65 ppm(s, CH_3).

Anal. calcd for $C_{16}H_{18}MoO_5S_2Se$: C, 36.30; H, 3.43.

Found : C, 36.54; H, 3.51.

Reaction of 2d with Bromine. To a methylene chloride solution of 2d(0.2 mmol) was added two molar amounts of bromine in methylene chloride. After 10 min, this was poured into 2 % $Na_2S_2O_3$ aqueous solution, extracted with methylene chloride, and washed with water. After drying with Na_2SO_4, this solution was evaporated and residue was crystallized from methylene chloride/ether, affording colorless crystals of 8a in 74 % yield: mp. 210°C; IR(KBr): 2970, 1905, 1576, 1445, 1403, 1367, 1343, 1320, 1205, 1173, 1165, 1136, 1022, 885, 637 cm^{-1}; PMR($CDCl_3$): δ 4.30 - 3.60(m, CH), 1.45 ppm(d, CH_3).

Anal. calcd for $C_{15}H_{28}Br_2N_2$: C, 45.47; H, 7.12; N, 7.07.

Found : C, 45.27; H, 7.01; N, 6.83.

Reaction of 2d with Acids. To a methylene chloride solution of 2d(0.2 mmol) was added large excess amounts of $(HNEt_3)\cdot CH_3CO_2$. After stirring for 2 h, this was poured into 50 ml of water, extracted with methylene chloride, dried(Na_2SO_4), and evaporated to dryness. The residue after recrystallization from methanol/ether afforded colorless crystals of 8b in quantitative yield. Similarly 2d treated with 30 % $HClO_4$ aq. and CH_3CO_2H gave 8b quantitatively.

Reaction of 2h and j with $HClO_4$. To a methylene chloride solution of 2h(0.2 mmol) was added large excess amounts of 70 % aq. $HClO_4$. After stirring for 2 h, this was washed, dried(Na_2SO_4), and evaporated to dryness. Removal of $Mo(CO)_6$ under reduced pressure and crystalliza-

tion from methanol afforded pale yellow crystals of 9a in 68 % yield: mp. 79°C; IR(KBr): 3105, 2960, 1863, 1499, 1460, 1413, 1376, 1260, 1189, 1160, 1090, 800 cm^{-1}; PMR($CDCl_3$): δ 9.04(s, C_{ring}- H), 3.48, 3.34(sep, NCH_3), 1.67 ppm(s, CCH_3); ^{13}C NMR($CDCl_3$): δ 146.9, 145.7(C_{ring}- N, C_{ring}- S), 125.3(C_{ring}- H), 52.8($\underline{C}CH_3$), 47.2, 42.5(NCH_3), 30.2 ppm ($C\underline{C}H_3$).

Anal. calcd for $C_9H_{16}ClNO_4S$: C, 39.87; H, 5.90; N, 5.15.
Found : C, 40.07; H, 5.98; N, 5.19.

By quite similar manner pale yellow crystals of 9b were obtained in 44 % yield: mp. 88°C; IR(KBr): 3080, 2970, 1843, 1597, 1580, 1549, 1512, 1483, 1447, 1375, 1357, 1300, 1229, 1180, 1090, 765, 688 cm^{-1}; PMR($CDCl_3$): δ 9.63(s, C_{ring}- H), 8.30 - 7.50(m, Ph), 3.90 - 4.65(br, NCH), 1.56, 1.52 ppm(d, CH_3); ^{13}C NMR($CDCl_3$): δ 144.5, 144.3(C_{ring}-N, $\underline{C}_{ring}$-C), 131.2(C_{ring}- H), 136.5, 130.6, 133.4, 120.2(Ph), 58.1, 55.0 (CH), 21.7 ppm(CH_3).

Anal. calcd for $C_{15}H_{20}ClNO_4$: C, 57.42; H, 6.42; N, 4.46.
Found : C, 57.11; H, 6.35; N, 4.72.

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CHAPTER 6

SPECTROSCOPIC STUDY ABOUT CYCLOPROPENYLIDENE (Cr, Mo, W) COMPLEXES

SUMMARY

The ground state electronic situation of several cyclopropenylidene transition metal (Cr, Mo, W) complexes are discussed with the use of infrared and ^{13}C-NMR spectra. At the same time the nature of bonding between carbene carbon and metal center are analyzed with the above complexes on the basis of infrared and ^{17}O-NMR data.

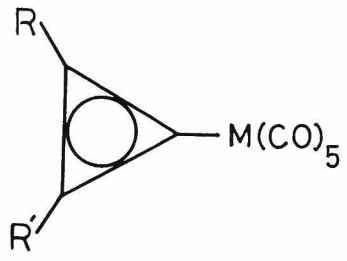
INTRODUCTION

Structures of cyclopropenylidene palladium complexes have become clear as described in Chapter 3 and 4. The first purpose of the reserch in this chapter is to interprete spectroscopic **evidence** obtained with cyclopropenylidene (Cr, Mo, W) complexes in correlation with that of cyclopropenylidene Pd complexes and their substituent effects on the C-3 ring system. The second purpose of this research is to clarify the nature of the bonding between cyclopropenylidene ligand and metal center.

So far CO stretching bands for C_{4v} pentacarbonyl complexes have been well studied on the basis of infrared spectra.[1] Such observation about CO stretching vibration may be utilized to the analysis of the bonding situation between cyclopropenylidene ligand and metal center. Similarly ^{17}O-NMR measurements may be a powerful tool for the elucidation of the bonding structure on 1.

RESULTS AND DISCUSSION

In the infrared spectra, bisaminocyclopropenylidene complexes 1 show two characteristic bands at 1830 - 1900 and 1470 - 1540 cm^{-1} (Table 1). The former corresponds to the C-3 ring deformation and the latter to the C_{ring} - N bond stretching vibrational bands. Both absorption bands are at lower frequencies compared to that of bisaminocyclopropenium cation 2. This trend is similar to that observed with bisaminocyclopropenylidene palladium complexes.[2,3] The lower frequency of the C_{ring} - N bond stretching band in 1 should reflect the more decreased



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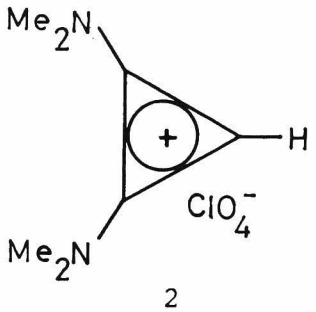
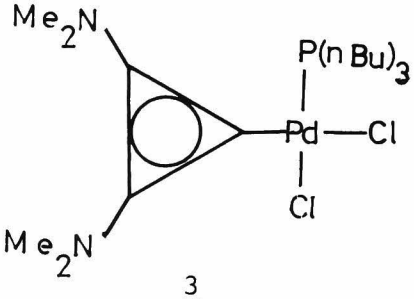


2

R	R'	M	
Me_2N	Me_2N	Cr	1a
Me_2N	Me_2N	Mo	1b
Me_2N	Me_2N	W	1c
$i\text{-}Pr_2N$	$i\text{-}Pr_2N$	Cr	1d
$i\text{-}Pr_2N$	$i\text{-}Pr_2N$	Mo	1e
$i\text{-}Pr_2N$	$i\text{-}Pr_2N$	W	1f
t-BuS	t-BuS	Cr	4a
t-BuS	t-BuS	Mo	4b
Ph	Ph	Cr	5a
Ph	Ph	Mo	5b
i-Pr	i-Pr	Cr	6a
i-Pr	i-Pr	Mo	6b
Me_2N	t-BuS	Cr	7a
Me_2N	t-BuS	Mo	7b
$i\text{-}Pr_2N$	Ph	Cr	8a
$i\text{-}Pr_2N$	Ph	Mo	8b

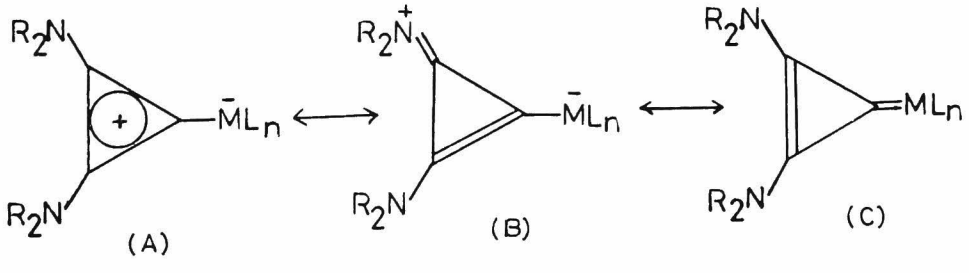


3

Table 1 The ring deformation and C_{ring}-N stretching absorption bands and ΔG_c to rotation about the C_{ring}-N bonds on 1a-f, 2, and 3.

	$\nu_{\Delta}(cm^{-1})$	$\nu_{C-N}(cm^{-1})$	ΔG_c(Kcal/mol)
1a	1899	1534	13.8
1b	1893	1534	14.1
1c	1892	1530	
1d	1834	1475	
1e	1836	1478	
1f	1836	1479	
2	1916	1615	18.8
3	1903	1557	15.4

multiple bonding character of this bond. The free energy of activation ΔG_c, which can be evaluated for C_{ring} - N rotation from ^{13}C-NMR measurements at varying temperatures, is estimated to be 13.8 and 14.1 Kcal/mol for 1a and b, respectively. These values are about 4 Kcal/mol less than that for 2. As has been discussed in the previous chapter, the decreased multiple bonding character of C_{ring} - N bond in 1 should be correlated with the considerable contribution of carbene form (C) which competes with form (B).



Furthermore ΔG_c of 1a and b are about 1 Kcal/mol less than that (15.4 Kcal/mol) for cis-dichloro(tri-n-butylphosphine)[bis(dimethylamino)-cyclopropenylidene]palladium 3. This may be attributed to more effective back donation from metal d-orbital to C-3 ring (π^*) of 1a and b compared to the case of 3.

In ^{13}C-NMR spectra, the complexes 1, 4, 5, and 6 exhibit four signals in the region of 130 - 230 ppm from TMS. These are attributable to the resonance of C-3 ring with four carbonyl carbons. Table 2 shows these chemical shifts. As observed with pentacarbonyl complexes LCr-$(CO)_5$, in general, only trans carbonyl carbon is more deshielded by 4 - 8 ppm than four cis carbonyl carbon of the present complexes. This reflects considerable σ electron donation from cyclopropenylidene ligand to the metal center.

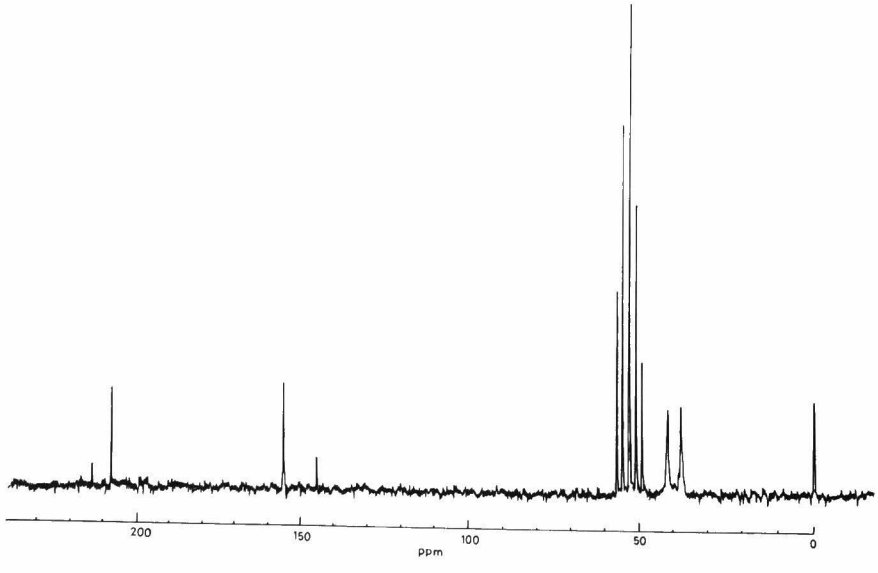


Fig. 1. ^{13}C-NMR spectrum of 1b.

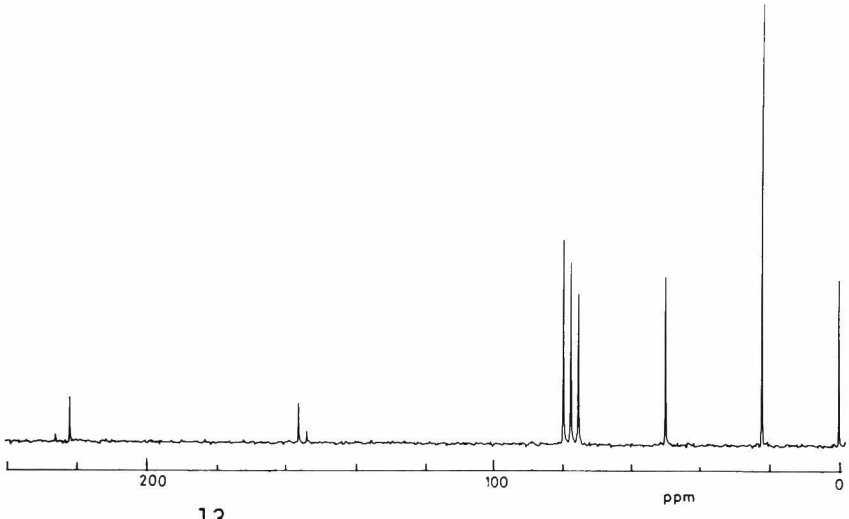


Fig. 2. ^{13}C-NMR spectrum of 1d.

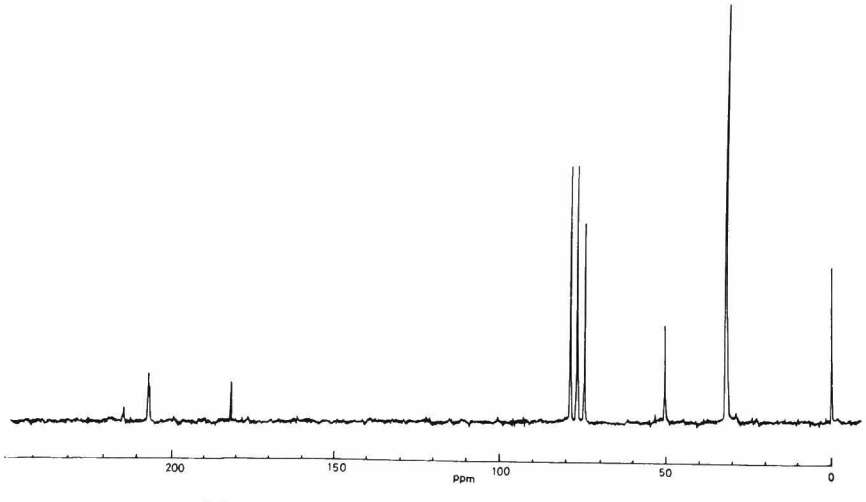


Fig. 3. ^{13}C-NMR spectrum of 4b.

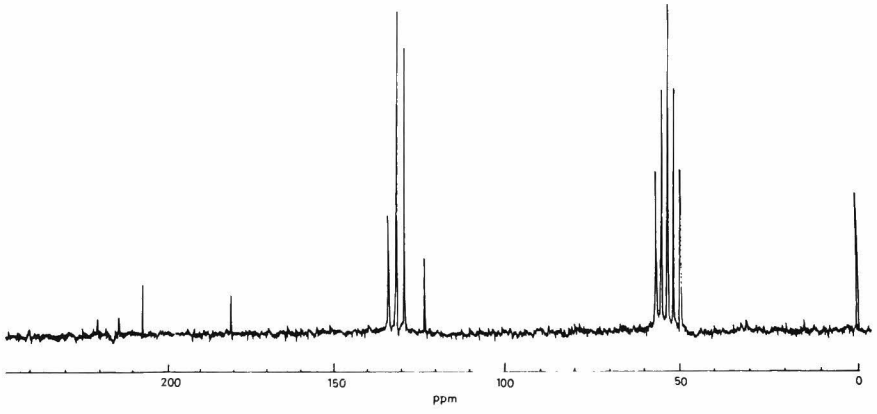


Fig. 4. ^{13}C-NMR spectrum of 5b.

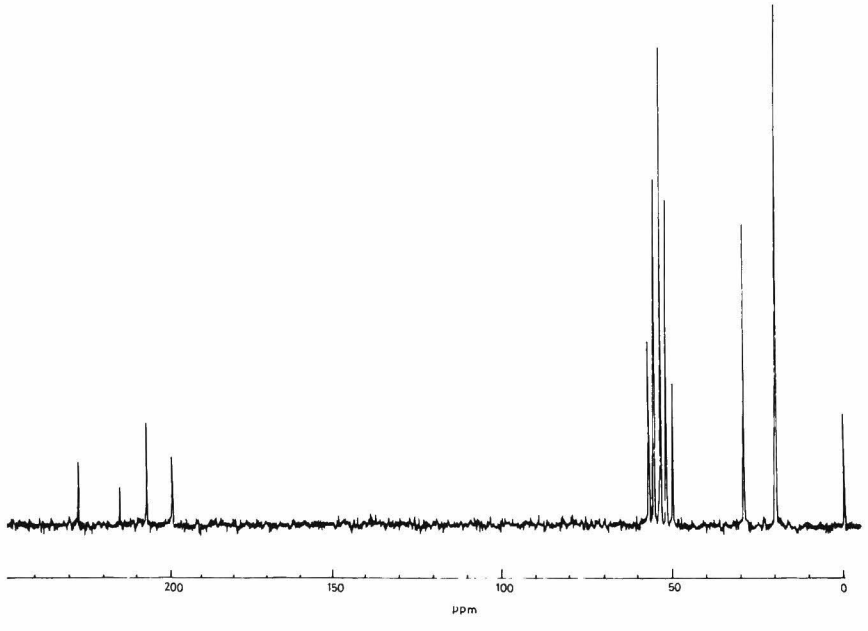
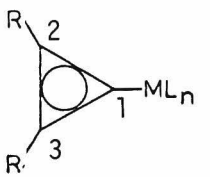


Fig. 5. ^{13}C-NMR spectrum of 6b.

Table 2 ^{13}C-Chemical shifts of C_3 ring and carbonyl carbons on the cyclopropenylidene complexes 1a-6b.

	R	M	C_1*)	C_2*)	Cis CO	Trans CO
1a	Me_2N	Cr	152.6	157.7	219.2	224.3
4a	t-BuS	Cr	212.5	181.8	217.4	223.2
5a	Ph	Cr	228.6	181.8	217.5	224.0
6a	i-Pr	Cr	236.3	200.1	218.3	222.4
1b	Me_2N	Mo	146.2	156.5	207.9	213.6
4b	t-BuS	Mo	205.4	181.2	205.7	212.7
5b	Ph	Mo	220.2	181.2	206.6	214.0
6b	i-Pr	Mo	227.5	199.1	206.9	214.5
1c	Me_2N	W	130.6	155.3	199.2	203.9

*) 

Carbene carbons of the complexes shown in Table 2 are relatively deshielded. For instance, the carbene carbon of 1a resonates at 152.6 ppm, while the ring carbons of 2 do at 138.1 and 96.1 ppm. According to Pople treatment,[5] the paramagnetic contribution to the screening constant can be represented as follows.

$$\sigma_p = -k/\Delta E(r^{-3})_{2p}(Q_{AA} + Q_{AB})$$

Such deshielding can be correlated with the lower values of average excitation energy ΔE and larger values of Q_{AB} of the paramagnetic term for the carbene carbon, which arise from the interaction between d-orbital of the metal and the carbene carbon. This kind of deshielding is commonly observed for carbene complexes.[6]

The C-3 ring carbons of cyclopropenylidene chromium complexes are shielded in the order of 1a (R= Me_2N) $\gg$ 4a (R= t-BuS) > 5a (R= Ph) > 6a (R= i-Pr). Quite similar order is observed with molybdenum complexes 1b - 6b. These suggest that electron densities on the C-3 ring carbons should increase in the order of bis(dimethylamino)cyclopropenylidene $\gg$ bis(t-butylthio)cyclopropenylidene > bisphenylcyclopropenylidene > bis-(i-propyl)cyclopropenylidene complexes. Since $|\sigma_p|$ increases with the increase of multiple bonding character of C_{ring} - metal bond, such a shielding order seems reasonable, because cobtribution of the canonical form (C) which competes with (B) may decrease in this order. Analogous shielding order was observed with the palladium complexes (see Chapter 4)...

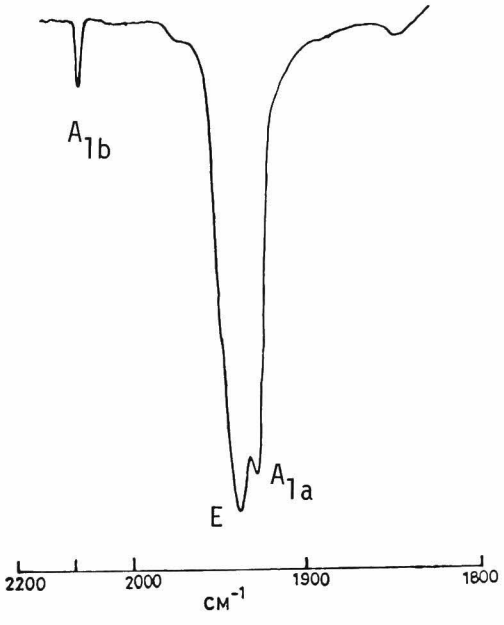


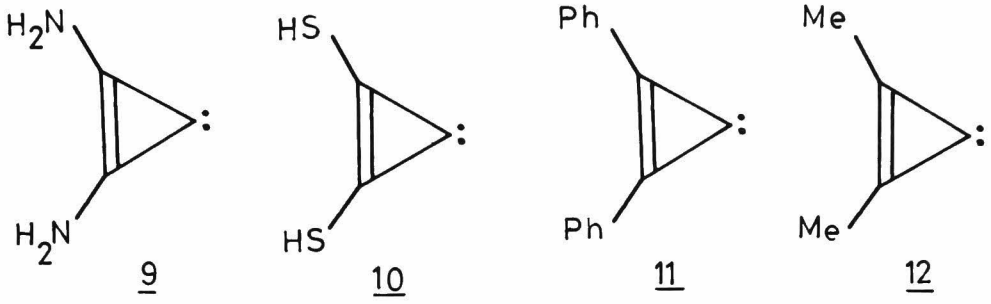
Fig. 6. Infrared spectrum of 1e in hexane.

With 1, 4, 5, and 6, it is possible to estimate bonding situation between carbene carbon and metal center from the analyses of infrared absorption bands for carbonyl stretching vibration. In hexane solution, these complexes exhibit three absorption bands characteristic to C_{4v} pentacarbonyl complexes.[7] The strongest absorption one is assigned to the carbonyl stretching of E mode and two medium absorption bands are to that of two A_1 modes. The stronger (A_{1a}) of the two A_1 bands is derived from the vibration of the single carbonyl group at a trans position to cyclopropenylidene ligand. Table 3 shows that frequency of this band increases along the series of ligands, bis(dimethylamino)-cyclopropenylidene, di-i-propylamino-phenylcyclopropenylidene, dimethyl-amino-t-butylthiocyclopropenylidene, bis(t-butylthio)cyclopropenylidene,

Table 3 The frequencies of CO stretching bands on 1a-8b in hexane.

	R	R'	M	A_{1b}	E	A_{1a}
1a	Me_2N	Me_2N	Cr	2063	1932	1926
7a	Me_2N	t-BuS	Cr	2070	1934	1934
8a	i-Pr_2N	Ph	Cr	2070	1938	1931
4a	t-BuS	t-BuS	Cr	2077	1945	1937
5a	Ph	Ph	Cr	2070	1945	1945
6a	i-Pr	i-Pr	Cr	2076	1944	1940
1b	Me_2N	Me_2N	Mo	2065	1931	1923
7b	Me_2N	t-BuS	Mo	2065	1932	1932
8b	i-Pr_2N	Ph	Mo	2065	1934	1927
4b	t-BuS	t-BuS	Mo	2065	1946	1937
5b	Ph	Ph	Mo	2065	1944	1944
6b	i-Pr	i-Pr	Mo	2064	1940	1940
1c	Me_2N	Me_2N	W	2060	1922	1922

bis(i-propyl)cyclopropenylidene, and bisphenylcyclopropenylidene, with both chromium and molybdenum complexes. This trend can be interpreted in terms of the relative charge-donating power of these ligands.[1)] Because of the directional nature of the hybrid metallic bonding orbital the carbonyl group trans to the cyclopropenylidene ligand should receive the largest part of the charge donated to the metal through bond formation. Such an accumulation of charge on the trans CO can produce a greater mixing of π- and π^*-orbitals of this group than in the case of four cis CO which receive relatively little of the charge. Therefore a ligand which possesses greater charge-donating ability should lower the carbon - oxygen bond order of the trans CO and, consequently, the frequency of A_{1a}. The charge-donating ability of cyclopropenylidene ligand



9 10 11 12

can be correlated with the net charge density at the carbene carbon. There are fair correlation between the net charge densities at carbene carbons of cyclopropenylidene models (9, 10, 11, 12) and frequencies of A_{1a} bands of 1 - 6 (see Chapter 1).

On the other hand the strongest band E which is assigned to the degenerated stretching vibration of four cis carbonyl groups can be affected by the charge acceptability of the cyclopropenylidene ligand. When the ligand has greater acceptability for the metallic charge, there exists possibility that the more charge may be withdrawn from the four cis carbonyl groups. This causes higher frequency of E. In Fig. 7 frequencies of A_{1a} are plotted vs. those of E with two series of chromium and molybdenum complexes discussed here. In these series bisaminocyclopropenylidene is expected to possess the strongest σ-charge donating ability and the least π-charge acceptability, while the reverse could be true with bisphenyl- and bis(i-propyl)cyclopropenylidenes. The frequencies of A_{1a} and E of Wanzlic type carbene complex, pentacarbonyl(N,N'-dimethylimidazoiline-2-ylidene)chromium 13[8] are also plotted in Fig. 7. Compared to 13 cyclopropenylidene complexes

Table 4 Lamor frequencies and chemical shifts of ^{17}O on 1b - 8b, and $M(CO)_6$.

Compd.				Lamor Frequencies* (12.10 MHz +, KHz)		Chemical Shifts (ppm from D_2O)	
	R	R'	M	Cis CO	Trans CO	Cis CO	Trans CO
1b	Me_2N	Me_2N	Mo	51.5063	51.5297	360.0	361.9
1e	i-Pr_2N	i-Pr_2N	Mo	51.5156	51.4057	360.7	355.9
7b	Me_2N	t-BuS	Mo	51.5297	51.5630	361.9	364.7
8b	i-Pr_2N	Ph	Mo	51.5316	51.6059	362.0	368.2
4b	t-BuS	t-BuS	Mo	51.5439	51.6410	363.1	371.1
5b	Ph	Ph	Mo	51.5439	51.7171	363.5	376.9
1d	i-Pr_2N	i-Pr_2N	Cr	51.6156	51.6117	369.0	368.7
1f	i-Pr_2N	i-Pr_2N	W	51.4806	51.4178	357.9	352.7
	$Cr(CO)_6$			51.7011		376.0	
	$Mo(CO)_6$			51.5952		367.3	
	$W(CO)_6$			51.4829		368.1	

*) All Lamor frequencies are measured at 21,100 Gauss magnetic field.

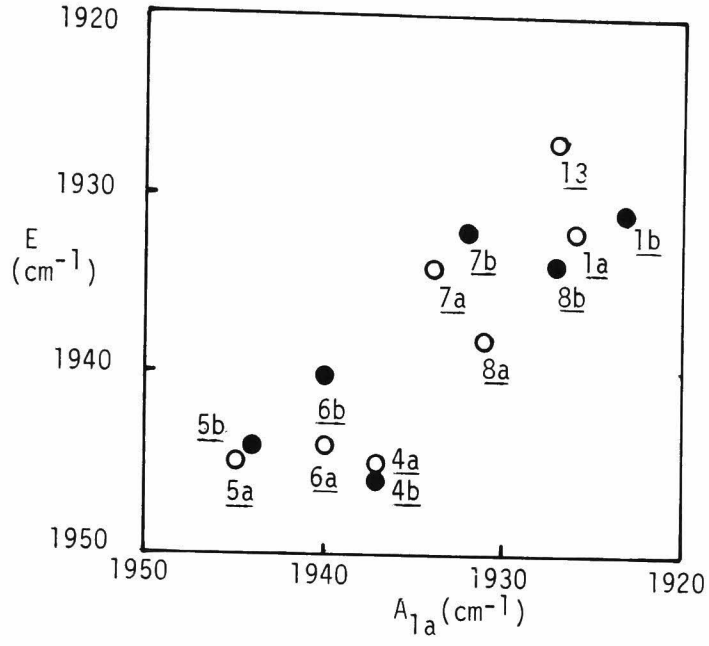


Fig. 7. Plots of frequencies of CO stretching E bands vs. that of CO stretching A_{1a} bands for Cr complexes(O) and Mo complexes(●).

(except 1a and b) show higher frequencies of A_{1a} and E. This suggests that the cyclopropenylidene ligands have less charge donating power through the hybrid metallic bond (except 1a and b) and more charge acceptability for back donation from the metal through d - π* interaction than is the case of such a Wanzlic type carbene, i.e., N,N'-dimethyl-imidazoiline-2-ylidene ligand.

The trend observed with CO stretching vibration (Fig. 7) are also seen with ^{17}O-chemical shifts of carbonyl ligands. The Lamor frequencies at 21,100 Gauss magnetic field and chemical shifts from H_2O are listed in Table 4, and Lamor frequencies of trans CO are plotted vs. those of cis CO in Fig. 8. The greater charge donation of the cyclo-

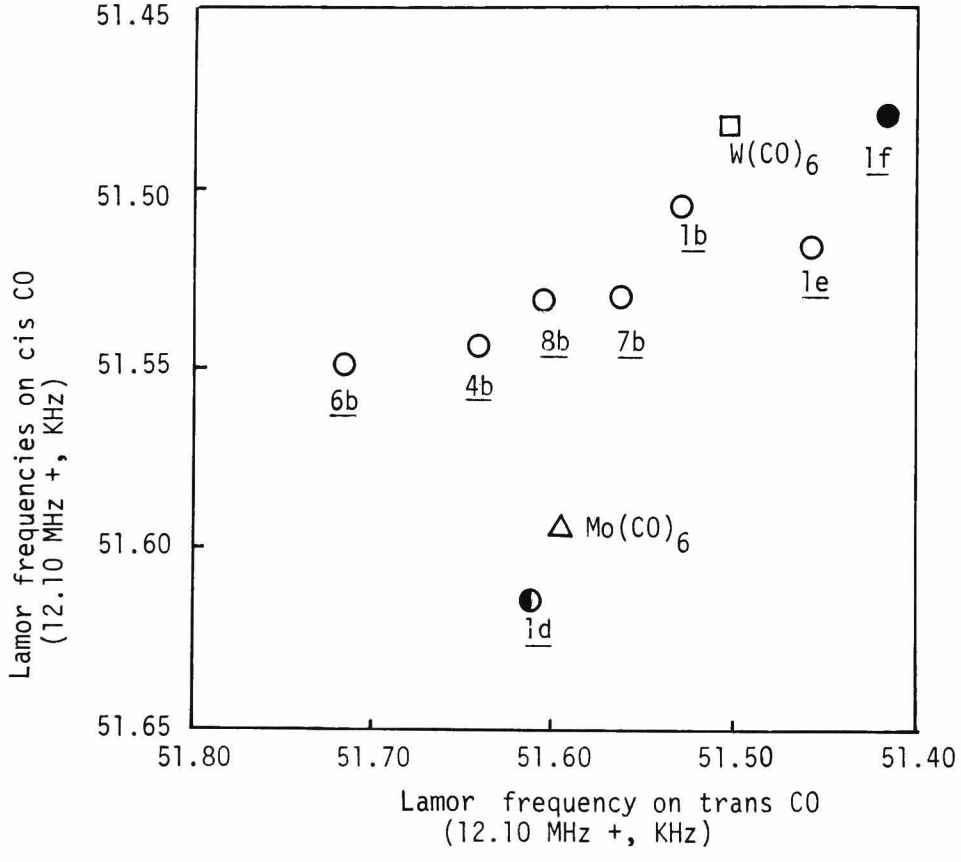


Fig. 8. Plots of Lamor frequencies of ^{17}O on cis CO vs. that on trans CO for cyclopropenylidene complexes and $M(CO)_6$.

propenylidene ligand should be responsible for the more shielding of the trans carbonyl oxygen, while the higher charge acceptability of the cyclopropenylidene ligand should cause the more deshielding of four cis carbonyl oxygens. Fig. 8 exhibits similar trend as that shown in Fig. 7. At the same time, it is interesting that the series of group VI b metal (Cr, Mo, W) complexes of bis(di-i-propylamino)cyclopropenylidene exhibit a linear correlation (Fig. 8).

Cyclopropenylidene ligands in Figs. 7 and 8 can be classified into three groups. They are bisaminocyclopropenylidenes, monoaminocyclopropenylidenes, and the other cyclopropenylidenes. This suggests dominant effects of amino substituent on the bonding situation between cyclopropenylidene ligand and metal center. Bisaminocyclopropenylidene has the greatest charge donating power and the least back charge acceptability, and cyclopropenylidene which has no amino substituent possesses the least charge donating power and the highest back charge acceptability in the series of cyclopropenylidene complexes discussed here.

EXPERIMENTAL

The infrared spectra were recorded on a Hitachi Model G 3 spectrometer. ^{13}C- And ^{17}O-NMR measurements were performed on a JEOL FX 90Q spectrometer.

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CHAPTER 7

^{195}Pt- AND ^{95}Mo-NMR SPECTRA OF BISAMINOCYCLOPROPENYLIDENE TRANSITION METAL COMPLEXES

SUMMARY

^{195}Pt- And ^{95}Mo-NMR spectra have been measured for several bisaminocyclopropenylidene complexes for the first time. The location of these resonance in ^{195}Pt and ^{95}Mo resonance fields, and the application of these spectra for the structural research are described in connection with the results from ^{31}P-NMR spectra.

INTRODUCTION

^{195}Pt-Chemical shifts, like those of other heavy nuclei, cover a wide range[1,2] and are sensitive to the ligands present in the co-ordination sphere and even to their arrangement. However there has been some difficulty for the direct measurements of ^{195}Pt resonance because of its relatively low sensitivity. Therefore, ^{1}H (^{195}Pt) INDOR technique has been used for the measurements of ^{195}Pt resonance[3] in the most of reports. In ^{1}H (^{195}Pt) INDOR spectra, the ^{1}H - ^{1}H coupling within the ligands sometimes interferes the resolution of these spectra.

In this chapter ^{195}Pt resonance of some complexes containing high strained organic ligands such as cyclopropenylidene are described, together with ^{31}P-NMR spectra. All ^{195}Pt resonances described here were measured directly by use of a Fourier transform NMR instruments. ^{95}Mo resonances of cyclopropenylidene Mo complexes were also measured and discussed. Nolle and his co-workers reported the shifts of several thousands ppm for ^{95}Mo nucleus.[4,5] Such a wide chemical shifts were also observed with NMR spectra of chromium[6] and tungsten.[7]

RESULTS AND DISCUSSION

^{195}Pt-NMR Spectra

The chemical shifts and J(^{195}Pt - ^{31}P) are summarized for some bis-aminocyclopropenylidene complexes 1a - d in Table 1 and these chemical shifts are illustrated in Fig. 1 together with those of other several Pt complexes. Here H_2PtCl_6 was used as an external standard and a

Table 1 ^{195}Pt-Chemical shifts and ^{195}Pt - ^{31}P coupling constants on cyclopropenylidene complexes and related compounds.

Compd.		^{195}Pt(ppm)	J(^{195}Pt - ^{31}P)(Hz)
$(i\text{-}Pr_2N)_2C_3$-Pt($P^a(n\text{-}Bu)_3$)($P^b(n\text{-}Bu)_3$)Cl, ClO_4^-	1a	-4441	3568(Pt - P^a) 2205(Pt - P^b)
$(i\text{-}Pr_2N)_2C_3$-Pt($P(n\text{-}Bu)_3$)($P(n\text{-}Bu)_3$)Cl, ClO_4^-	1b	-4321	2344
$(i\text{-}Pr_2N)_2C_3$-Pt($P^a(n\text{-}Bu)_3$)($P^b(n\text{-}Bu)_3$)I, ClO_4^-	1c	-4789	3449(Pt - P^a) 2228(Pt - P^b)
$(i\text{-}Pr_2N)_2C_3$-Pt(I)(I)(2)	1d	-4720	
Cl-Pt($P(n\text{-}Bu)$)($P(n\text{-}Bu)_3$)Cl	2a	-4450	3515
Cl-Pt($P(n\text{-}Bu)_3$)($P(n\text{-}Bu)_3$)Cl	2b	-3921	2383
Ph-Pt($P^a(n\text{-}Bu)_3$)($P^b(n\text{-}Bu)_3$)Cl	3a	-4426	4208(Pt - P^a) 1616(Pt - P^b)
Ph-Pt($P(n\text{-}Bu)_3$)($P(n\text{-}Bu)_3$)Cl	3b	-4268	2773

* All chemical shifts are referred to H_2PtCl_6 in D_2O.

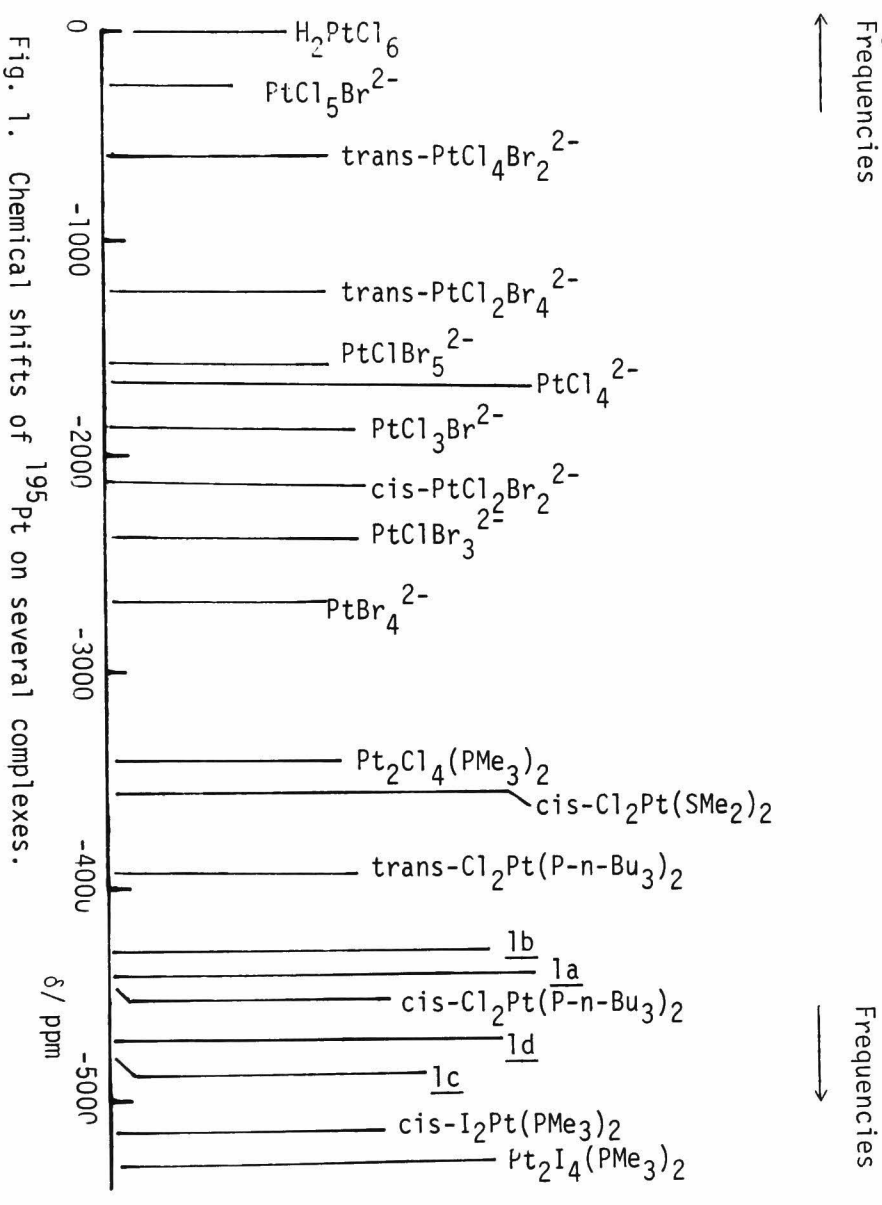

Fig. 1. Chemical shifts of ^{195}Pt on several complexes.

Table 2 ^{31}P-Chemical shifts and ^{31}P - ^{195}Pt coupling constants on 1a - 2b.

Compd.	δ ^{31}P(ppm)	$J(^{31}P - ^{195}Pt)$(Hz)
1a	27.4 (P^a)	3562 (P^a- Pt)
	33.9 (P^b)	2207 (P^b- Pt)
1b	36.8	2344
1c	24.6 (P^a)	3452 (P^a- Pt)
	26.1 (P^b)	2232 (P^b- Pt)
2a	31.5	3521
2b	35.0	2383

* All chemical shifts are referred to n-Bu_3P in $CDCl_3$.

negative shift means a shift to lower frequency. The ^{195}Pt chemical shifts of cyclopropenylidene complexes are located in the region for Pt^{II} - phosphine complexes. In particular, the chemical shift of 1a is close to that of cis-$(n\text{-}Bu_3P)_2PtCl_2$. These suggest that the electron density at the Pt atom do not change so much among 1a - d and Pt^{II}-phosphine complexes in general.

Frequently ^{195}Pt-chemical shifts are affected significantly by the configuration of the complexes. For instance, ^{195}Pt of trans-$(n\text{-}Bu_3P)_2$-$PtCl_2$ is deshielded by ca. 530 ppm from that of cis-$(n\text{-}Bu_3P)_2PtCl_2$. Compared to this, the chemical shift difference between the cis and trans isomers is relatively small(ca. 120 ppm) for bisaminocyclopropenylidene complexes. The chemical shifts of the complexes(1a, 1b, and

2a) in which at least one phosphine or cyclopropenylidene ligand is coordinated in the cis position to the other phosphine ligand are relatively close to each other.

It is well known that iodine ligands cause more shielding on ^{195}Pt than chlorine ligands do in the case of Pt^{II} planar complexes and the upfield shifts induced by substitution of chlorine ligand for iodine ligand can be shown fairly quantitatively.[8] For instance, $[PtI(PMe_3)_3](NO_3)$ is 256 ppm more shielded than $[PtCl(PMe_3)_3](NO_3)$.[8] In cyclopropenylidene complexes too, 1c is ca. 350 ppm more shielded than 1a.

The ^{195}Pt signals of 2a and b appear as a triplet at -4450 and -3921 ppm, respectively. In these complexes, as are seen in the most cases of Pt^{II}- phosphine complexes, very large Pt - P coupling constants are observed. Such coupling are also observed in ^{31}P-NMR spectra of them (Table 2). ^{31}P Signal of 2a appears in down field lower by 31.5 ppm from that of free $n\text{-}Bu_3P$ as a pair of a singlet and a doublet. The latter is due to the coupling of phosphorous nucleus and naturally abundant ^{195}Pt nucleus. These $J(^{195}Pt - ^{31}P)$ in Table 2 coincide with the corresponding values in Table 1 within experimental error. The values of $J(^{195}Pt - ^{31}P)$ are considerably different between 2a and b. Coupling constants are larger in cis isomer than in trans isomer. This should be correlated with the differences of σ-bonding force and bond length between Pt and P atoms in the two isomers. In trans isomers two phosphine ligands which have larger trans influence than chlorine ligands are in trans position to each other. Consequently the Pt - P bonds of the trans isomer are weakened in comparison with the case of the cis isomer.

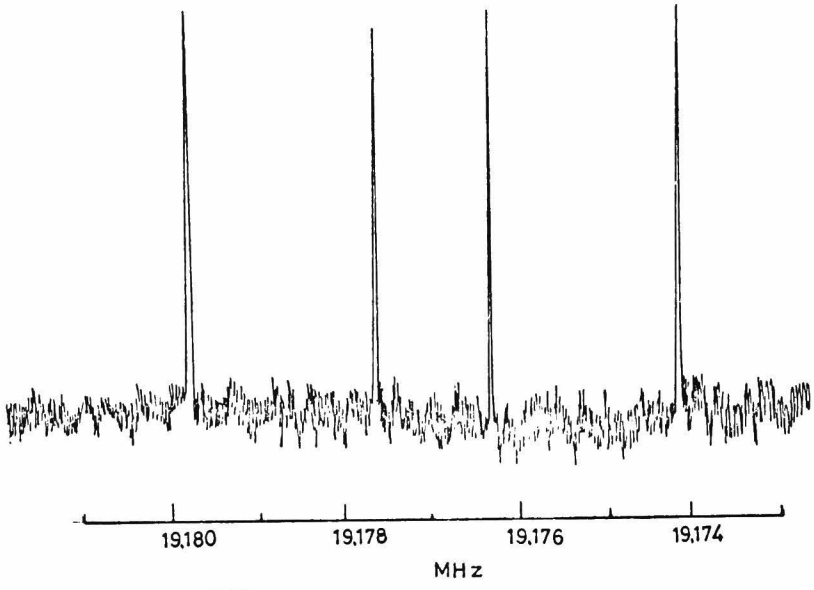

Fig. 2. ^{195}Pt-NMR spectrum of 1a.

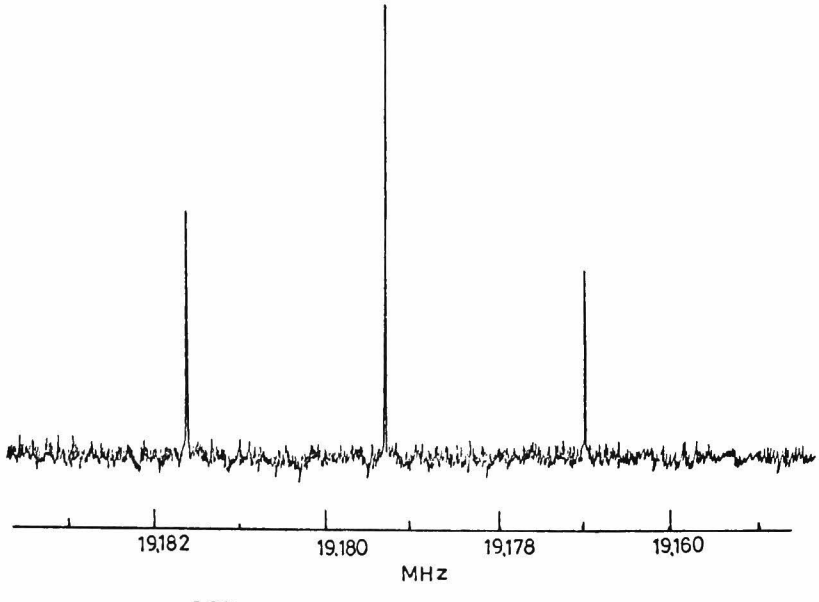

Fig. 3. ^{195}Pt-NMR spectrum of 1b.

The value of $J(^{195}Pt-^{31}P)$ should be very useful for the estimation of the trans influence of a variety of ligands on phosphine ligand. So far, the influence of ligands on trans halogen ligand has been well studied[9] by means of far-infrared spectra, but there have been few reports with the trans influence on π-charge acceptive ligands, such as phosphine, etc. The value $J(^{195}Pt-^{31}P)$ can be taken as a guide to the estimation of the ligand influence on such trans ligands of π-charge acceptable type, regarding Pt complexes in general. From $J(^{195}Pt-^{31}P)$ values shown in Table 1, such trans influence is in the order of Ph > $(i\text{-}Pr_2N)_2C_3$: ≃ $(n\text{-}Bu)_3P \gg Cl$. Since the trans influence of cyclopropenylidene ligand differ from that of chlorine ligand, cis and trans isomers of cyclopropenylidene complexes show different pattern of spectra to each other. ^{195}Pt-NMR spectrum of 1a exhibits a quartet signal(Fig. 2) at -4441 ppm while that of 1b shows a triplet signal(Fig. 3) at -4321 ppm.

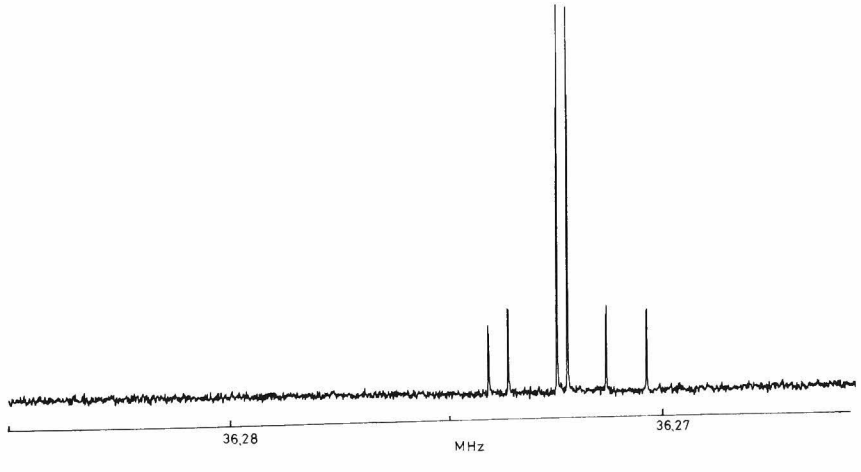

Fig. 4. ^{31}P-NMR spectrum of 1a .

Similarly, ^{31}P-NMR spectrum of 1a is very different from that of 1b. Instead of a simple pair of singlet and doublet signals in 1b, the phosphorous nuclei of 1a shows fairly complicated spectrum (Fig. 4), in which two different direct couplings between ^{195}Pt and ^{31}P nuclei and a geminar coupling between two ^{31}P nuclei are observed. Also in ^{195}Pt- and ^{31}P-NMR spectra of 3a and b, similar patterns of signals are observed.

Thus ^{195}Pt-NMR spectra are very useful for the structural study of these platinum complexes.

^{95}Mo-NMR Spectra

^{95}Mo-NMR spectra of diverse cyclopropenylidene complexes were measured directly on a Fourier transform NMR instrument at 21,100 Gauss magnetic field. Kautt and his co-workers suggested that ^{95}Mo has a relatively small quadrapole moment and hence measurement of ^{95}Mo in some less symmetrical complexes should also be possible.[4] ^{95}Mo-NMR spectra of several cyclopropenylidene complexes in Table 3 show very sharp signal lines. The line width on 4a is less than 5 Hz (Fig. 5). This is considerablly small compared to the line width on $K_2Mo(CN)_8$ (75 Hz)[5] and $(NH_4)_6$-Mo_7O_{24} (> 150 Hz; Fig. 6). Taking account of that of highly symmetrical Mo(CO being 0.7 Hz, the central molybdenum atoms in cyclopropenylidene complexes might have fairly high symmetry.

^{95}Mo-Chemical shifts of several cyclopropenylidene complexes 4a - e and some related compounds are shown in Table 3 where every chemical shift is referd to $Mo(CO)_6$ in $CDCl_3$ and a positive shift means a shift to higher frequency. At the same time, Fig. 7 exhibits the chemical

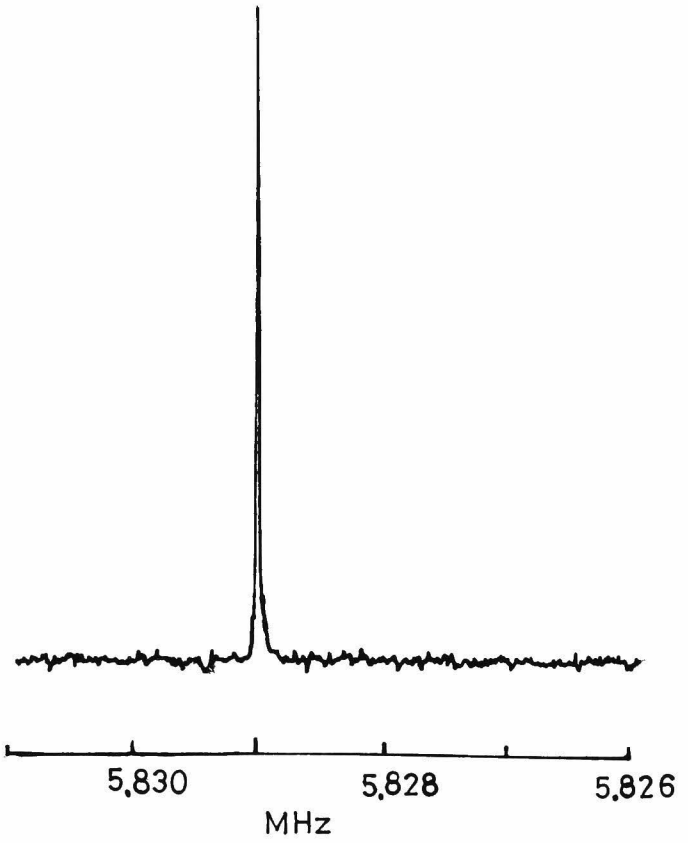

Fig. 5. ^{95}Mo-NMR spectrum of 4a in $CDCl_3$.

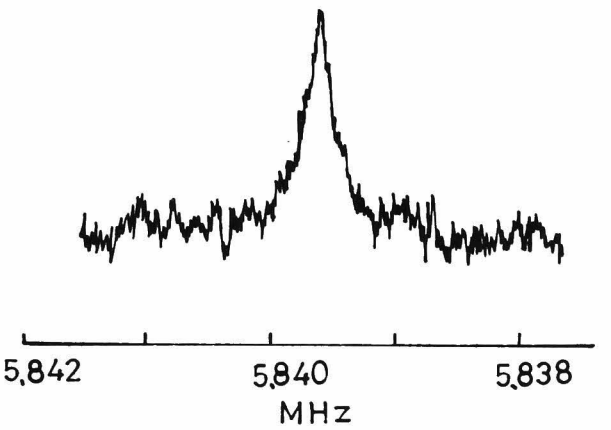

Fig. 6. ^{95}Mo-NMR spectrum of $(NH_4)_6Mo_7O_{24}$ in D_2O.

Table 3 Lamor frequencies and chemical shifts of ^{95}Mo on cyclopropenylidene complexes and some relared compounds.

	Compd.	Lamor Frequency (Hz)	Chemical Shift (Hz)	(ppm)	Solv.	
	$Mo(CO)_6$	5,828,573.2	0	0	$CDCl_3$	this work
4a	$(Me_2N)_2C_3Mo(CO)_5$	5,828,735.3	162	27.8	$CDCl_3$	this work
4b	$Ph(i\text{-}Pr_2N)C_3Mo(CO)_5$	5,828,903.9	331	56.8	$CDCl_3$	this work
4c	$t\text{-}BuS(Me_2N)C_3Mo(CO)_5$	5,829,008.3	435	72.6	$CDCl_3$	this work
4d	$(t\text{-}BuS)_2C_3Mo(CO)_5$	5,829,141.4	568	95.5	$CDCl_3$	this work
4e	$Ph_2C_3Mo(CO)_5$	5,829,027.9	455	78.8	$CDCl_3$	this work
	K_2MoO_4			1856	H_2O	ref 5.
	$K_2Mo(CN)_8$			547	H_2O	ref 5.
	K_2MoS_4			2352	H_2O	ref 5.
	$(NH_4)_6Mo_7O_{24}$	5,839,618,3	11045	1891	D_2O	this work

* All chemical shifts are referred to $Mo(CO)_6$ in $CDCl_3$; a positive shift means a shift to higher frequency.

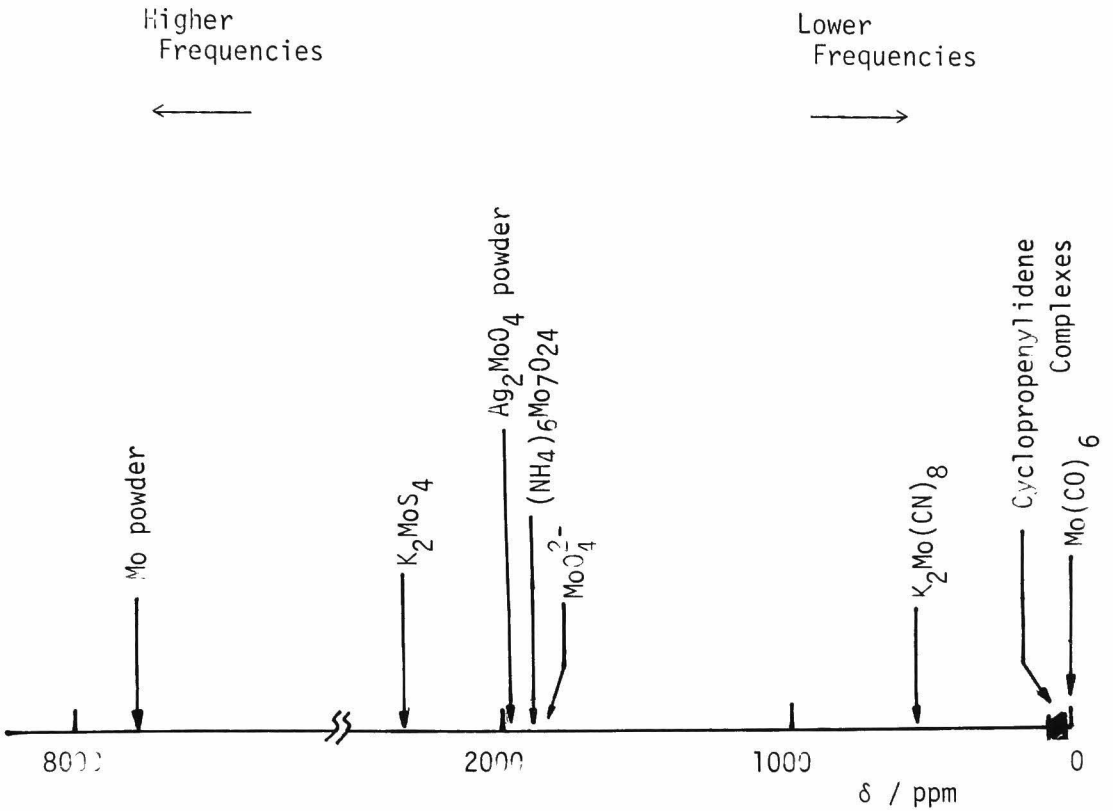

Fig. 7. Chemical shifts and Knight shift of ^{95}Mo.

shifts of these compounds. The ^{95}Mo signals of 4a - e appear in the region of 20 - 100 ppm. These should be located in the region of zerovalent molybdenum complexes represented by $Mo(CO)_6$. Compared to this, hexavalent molybdenum complexes are in lower region where K_2MoS_4 is one of the most deshielded.[4] The chemical shifts of cyclopropenylidene complexes are deshielded in the order of 4d > 4e > 4c > 4b > 4a. Such an order is in fair agreement with that observed with infrared vibrational bands for C = O stretching and with ^{17}O-chemical shifts of carbonyl oxygens of several cyclopropenylidene pentacarbonyl complexes (see Chapter 6). As was discussed by Ramsey,[10] main contribution to the shielding of a heavy-metal nucleus such as ^{95}Mo should be the paramagnetic term where the excitation energy and coefficients of metal d-orbitals are one of the most significant factor. Therefore the ligand - metal interaction seems to affect significantly the chemical shift of ^{95}Mo. Above shielding order on 4a - e may be correlated with the $p\pi - d\pi$ interaction between cyclopropenylidene ligand and ^{95}Mo as was discussed in previous chapter.

EXPERIMENTAL

^{195}Pt-, ^{31}P-, and ^{95}Mo-NMR spectra were recorded on a JEOL FX 90Q spectrometer. For ^{195}Pt- and ^{95}Mo-NMR measurements, pulse repetition rate (PR), pulse width (PW), number of pulse (NP), and spectral width (SW) were set as follows,

	PR(Hz)	PW(μs)	NP	SW(Hz)
^{195}Pt	1	10	10000	20000
^{95}Mo	11	200	50000	5000 - 20000

The standard compound H_2PtCl_6 / H_2O and $Mo(CO)_6$ / $CDCl_3$ were observed at Lamor frequencies of 19.262 539 6 and 5.828 573 2 MHz, respectively.

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7. ^{195}Pt- and ^{95}Mo-NMR Spectra of Cyclopropenylidene Transition Metal Complexes

Z. Yoshida and Y. Kamitori

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